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Ukrainian Materials Science Society

6TH INTERNATIONAL SAMSONOV CONFERENCE

"MATERIALS SCIENCE
OF REFRACTORY COMPOUNDS"

The Conference is dedicated to the centenary of the birth of
GRIGORII VALENTINOVICH SAMSONOV

May 22-24, 2018
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<u>Plenary</u>

REINFORCED CERAMIC MATERIALS

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The solution of the problem of heat resistance and wear resistance today is associated with the creation, production and use of materials based on refractory compounds.

Ceramic materials have the highest theoretical values of strength, hardness and heat resistance.

Ceramic materials based on borides, carbides, silicides, oxides, nonmetallic refractory compounds (silicon carbide, boron and boron nitride) have a number of advantages over refractory metals and alloys.

Ceramic materials have:

a high melting point, hardness and chemical stability at ultrahigh temperatures;

a high homologous temperature of the beginning of intense creep of 0.5 - 0.8 Tmelt, while for metallic materials 0.2 - 0.3 Tmelt, which is only 500-750 °C;

low coefficient of thermal expansion in comparison with metallic materials.

However, their widespread introduction is limited by high fragility and low strength.

In addition, ceramics are difficult to handle and receive complex shape parts with given geometric dimensions, limiting its wide use in practice.

The investigation of the mechanisms of nucleation and growth of phase constituents of quasibinary eutectic alloys from refractory compounds, physicochemical foundations for controlling the microstructure of reinforced ceramic materials, which are a matrix from one refractory compound penetrated by uniformly distributed fibers of another refractory compound, are created.

It is proved that irrespective of the nature of the components of the eutectic alloy for the formation of the microstructure, the geometric dimensions and the number of reinforcing inclusions are affected by the minimum supercooling of the melt at the crystal growth front and, above all, its concentration component.

The mechanism of reinforcement reinforced by fibers, crystals of refractory compounds, obtained by crystallization of melts of eutectic alloys, is disclosed.

It is proved that high mechanical properties of composites at room temperatures are mainly due to the redistribution of the load between the matrix and the fibers.

The increase in the number and dispersion of fibers leads to an increase in the proportion of the load perceived by single-crystal fibers, the strength of which approximates the theoretical, due to the increase in the surface area, and the frictional force between the phase components of the composite.

It is proved that the high physical and mechanical characteristics of reinforced ceramic materials in a wide range of temperatures are due to the action of predominantly grain-boundary, deformation hardening mechanisms and the stress-strain state of fibers and matrix.

It is established that the increase in the strength of reinforced composite materials with increasing temperature is mainly due to the removal of elastic stresses in the phase constituents of the composite material.

It has been proved that ceramic reinforced materials need to be annealed in order to remove residual stresses formed during crystallization from melt or sintering.

It is shown that annealed ceramic composites will allow obtaining strength at the level of 1000 MPa at temperatures of 1600 °C and record high performance (250 MPa) at temperatures of 2000 °C.

It is shown that, by mechanical properties and operating temperatures, reinforced ceramic materials cover all classes of instrumental materials and high-temperature structural materials that are known to date, and can be effectively operated under extreme conditions of simultaneous action of large dynamic loads, high temperatures, high-speed heating, abrasive wear and aggressive environments.

NEW DIRECTIONS IN NANOSIZED PARTICLES AND FUNCTIONAL MATERIALS

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Although the scientific contribution of Grigoriy Valentinovich Samsonov is certainly the highest to high temperature refractory materials, by writing a book with him on Activated Sintering in 1974 [1] I also met the other side of his interest: fine and ultrafine (nanosized) powders and their sintering with and without external fields. Therefore, my presentation will be devoted to nanosized particles and functional materials. The science and technology of nanosized particles has an enormous importance today in the world and is an area with a great potential for new technological advances, being the result of unique physical and chemical properties of these particles. Nanosized particles with highly controlled properties at molecular and nano levels developed in our laboratory will be reviewed in this lecture [2]. Numerous categories of nanoparticles that attract a wide interest from the scientific community were studied. Examples describing the preparation of multifunctional nanosized particles (gold, magnetic nanocomposites, undoped and doped calcium phosphates, ZnO, SiC, lithium cathode particles, biodegradable polymers, various hybrid metal-ceramic-polymer nanocomposites) will be presented. Special attention will be paid to the fabrication of full density nanostructured materials from nanosized particles without the influence of external field during sintering. Broad classes of functional materials, including engineering, electronic, energy, catalytic, biomedical and pharmaceutical will be considered. By exploiting the extreme condition of high fluxes, fields and forces, complex chemistries and molecules and interfacial systems will accelerate the materials discovery [3]. As Grigoriy Valentinovich deemed, searching for new properties and applications of materials should be done in the poorly charted regions of the Periodic Table. A testimony to the overarching relevance of this claim are high-Tc superconductors, perovskite solar photovoltaics, graphene and other 2D materials, quantum materials, et cetera.

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PRESSING AND SINTERING POWDERS
OF REFRACTORY COMPOUNDS

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On the initiative of Grigorii Valentinovich Samsonov at the Institute of Metal Ceramics and Special Alloys of the Academy of Sciences of the Ukrainian SSR (since 1964 the Institute for Problems of Materials Science of the National Academy of Sciences of Ukraine), research directions have been developed for the synthesis of powders of metal-like and non-metallic refractory compounds and the development of materials based on them. In these areas, research on the pressing and sintering of samples for the studies of physical and mechanical properties as well as new materials of a certain practical application have been given priority.

Formation of the structure and properties of sintered products from refractory compounds and materials based on them is connected with the random packing of particles of the starting powder. Because of the density fluctuations and the coordination (contact) number of particles in the volume of the initial porous preform, a meso-structure arises in it, each element of which consists of a core with a random dense packing of particles and a shell with a loosened packing and low coordination numbers of the particles. Mesostructure formed at the initial stage of the technological process of obtaining the material is inherited at its subsequent stages and during sintering is manifested as the zonal isolation caused by the difference in the coordination number of particles, and consequently, the sintering forces in the nuclei and shells (boundaries) of the mesoelements. The effect of zonal isolation can be reduced by applying external pressure.

Analysis of the compaction of the porous body during pressing and sintering is performed being based on the fundamental law of conservation of total energy in the mechanical system. This system consists of a machine whose working parts deform the porous body and as the deformation increases, the force in the system increases, as a reaction of the body's resistance to an external action, in which its rheological properties such as elasticity and viscosity are manifested. In the case of static effects, the change in the kinetic and potential energy of the system, because of their smallness, can be neglected. Therefore, analysis of the kinetics of densification during the sintering porous body is simplified when considering the body volume flow under the action of the Laplacian pressure due to the surface tension in the pores and the external pressure. The bulk viscosity of a porous body is proportional to the shear viscosity of the matrix forming the porous body, and depends nonlinearly on its relative density. Approximate formulas are used to express this relationship. The velocity of the bulk flow of a body formed by a viscous matrix is proportional to the pressure and inversely proportional to the bulk viscosity. To analyze the non-Newtonian flow of a matrix that obeys a power law, the method of root-mean-square of strain rates and stresses is used. Using the obtained dependences for the analysis of experimental data makes enable to estimate the fluidity and activation energy of the viscous flow of the matrix forming the porous body from the change in the relative density during densification of powders of refractory compounds and ceramic-metal materials based on them under isothermal and nonisothermal conditions of pressure sintering. Obtained values of activation energy indicate possible flow mechanisms.

Based on the rheological model of the mechanical interaction of a viscoelastic irreversibly compressible body with an impact machine with one degree of freedom, an analysis is made of the densification dynamics of the porous body under impact sintering. The impact on the deformable body is accompanied by a thermo- mechanical effect, which is manifested in an increase in temperature of the body. Depending on the energy of impact, body weight and its heat capacity, the temperature rise can be variated by the value from tens to hundreds of degrees. A small fraction of the impact energy is stored in the form of internal stresses.

Data on the pressing and kinetics of the sintering of powders of refractory compounds with pressure under isothermal and nonisothermal conditions are given, as well as the dynamics of compaction of porous compacts of hardmetals during impact sintering.

ULTRA-HIGH-TEMPERATURE CERAMICS: PROCESSES ON THE GRAIN BOUNDARIES AT SINTERING and PROPERTIES FORMATION

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Ultra-high-temperature ceramics (UHTC) has an increasing popularity in the world and, particularly, in Ukraine, for the problems of machines and units reliability in power engineering, aviation and space machinery used in the temperature range of 1600-2500 oC. The present work is devoted to the investigation of activated sintering processes and analysis of the structural state and structural sensitivity of the mechanical properties of ultra-high-temperature ceramics based on zirconium boride. The processes of phase interactions in the grain boundary zones with the determination of the grain-boundary strength characteristic and the relationship between grain-boundary strength and the mechanical properties of composites have been studied. The eutectic systems where, at solid-state sintering, the activation of sintering takes place have been considered. The activation is connected with the diffusion zones formation, phase interactions and transformations with an increased diffusion characteristics in the region of phase boundaries. Experimentally observed significant attenuation of interatomic bonds and an increase in the amplitude of the thermal vibrations of atoms are the physical cause of the diffusion activity in the boundary volumes of the phases of the systems under consideration, which stimulates an increase of the rate of a number of high-temperature processes (powders sintering, creep, etc.). The study of the structural sensitivity of the strength of the ceramics under investigation is carried out by measuring a wide range of mechanical characteristics, including grain-boundary strength. Indentation methods at high loads on the indenter, when contact fracture processes are developed in the penetration area have been used. Correlation dependences between the ceramics basic mechanical characteristics, first of all connecting grain-boundary strength with fracture toughness, compressive strength, flow stress, etc., have been found. It is the ground of the analysis of the brittle materials structural sensitivity of the mechanical properties, which determines the prospects for obtaining ceramics with the predetermined properties

SCIENTIFIC HERITAGE G.V. SAMSONOV IN THE FIELD OF CREATION OF INSTRUMENTAL AND WEAR-RESISTANT MATERIALS

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Grigory Valentinovich Samsonov, among the diverse areas of his activity, founded for the first time in Ukraine a scientific direction on the improvement of sintered cemented carbides (TCs) and the creation of new non-wolfram hard alloys, which were developed in the KPI in cooperation with the CF VNIITS starting in 1968. Thanks to the joint efforts of scientists and production conditions, the conditions for obtaining hard alloys based on titanium carbide with nickel and with nickel-molybdenum bonds have been studied, and experimental technology has been developed and x production [1]. Solid alloys of 70-80% Ti-30-20% Ni-Mo MNT and THM grades had a bending strength of 1150-1250 MPa with a hardness of 90-91 HRA. Their toughness was close in values for standard tungsten-containing cermets T15K6 and T5K10.

At the same time, research was conducted on the development of hard alloys based on other refractory compounds. Based on the developed G.V. Samsonov and his school of ideas on the nature of the electronic exchange between metal atoms and nonmetals, in particular in Me-C and Me-N vapor, with the formation of stable electronic configurations, developed TC based on titanium carbonitride with a nickel-molybdenum bond (Ni-80 % Mo, about 20%) with a bending strength of 1100-1350 MPa and a hardness of 89 to 90 HRA, which were comparable to properties of the T15K6 alloy.

As a result of the analysis of the world state at that time of work on metal-ceramic alloys carried out by G.V. Samsonov and his school formulated the main ways of developing TC.

Alloys based on titanium carbonitride grades KTNM30A and KTNM30B were developed. With an appropriate variation in the content of carbonitride TiCxNy and the binder, they could be used in processing a variety of materials, for the manufacture of various parts and accessories. Industrial production of various products was set at about 330 tons per year. They were used by many hundreds of industrial enterprises of Ukraine, Russia, Uzbekistan, etc.

In the framework of this direction, on the initiative of G.V. Samsonov for the first time carried out research on the development of technology for producing fused TC and the study of their properties. Later on, fundamental foundations were developed for the development of a number of materials involving fused TC for abrasive and magnetic abrasive processing, and the application of wear-resistant composite materials.

Developments in this direction were implemented at a number of enterprises: the Krivoy Rog turbine plant "Voskhod", the enterprise "Technical Chord" at NIDGHS, (Lyubertsy, Russia), the Navoinsky mining enterprise (Kazakhstan); With the participation of the department, plots were created to apply coatings to a number of enterprises.

Scientific results of the work carried out, the developed technologies were used in writing monographs and textbooks [2-4].

Thus, over the past 46 years, the scientific forecast of G.V. Samsonov on the creation of instrumental and wear-resistant materials was fully justified.

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STUDY OF MECHANICAL PROPERTIES
OF REFRACTORY COMPOUNDS

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Refractory compounds (RC) have a high melting temperature Tm, a high hardness and a high characteristic deformation temperature T* at which the resistance of the crystal lattice to the movement of dislocations (the Peierls-Nabarro stress) becomes significant and causes a sharp increase in the yield strength with decreasing temperature below T* (table 1).

Table 1. Properties of RC

Material	TiC	WC	ZrC	Al_2O_3	TiB_2
T_m, ^{o}C	3120	2850	3800	2050	2950
T*, ^{o}C	1890	1500	2185	1250	1070
HV, GPa	24	17,8	22	20	33
C	1,08	1,89	1,06	0,94	1,06
δ_H	0,46	0,81	0,46	0,41	0,51

Below T*, cold-brittleness is possible and standard mechanical tests are ineffective. In this wide temperature range, the indentation technique has been used successfully to study the mechanical properties of a RC. In the most brittle RC, two intervals are observed on the temperature dependence of hardness (Fig.1).
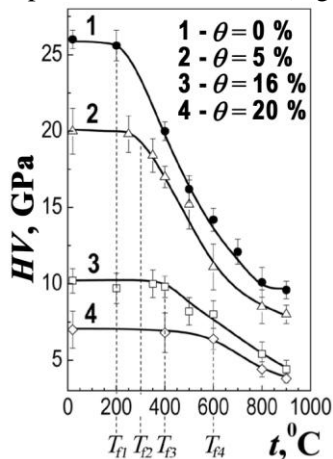

Fig.1. Effect on porosity on the temperature dependence of the hardness of SiC.

Tf1, Tf2, Tf3, Tf4 – temperature of a brittle-ductile transmission, respectively.

HM value and elastic characteristics [1]. For a RC, usually 1 <C <2.

The boundary between these intervals, the temperature Tf, can be regarded as the temperature of a brittle-ductile transition during indentation.

The yield stress σS is connected with the Meyer hardness HM by the ratio: HM=C·σS, where C is the Tabor parameter. The value of C and the yield strength are calculated from the

By the dependence of σS(T) determines the activation energy of dislocation motion and the activation volume and the Peierls-Nabarro stress can be determined.

The plasticity characteristic of the material δH can be calculated by the equation [2]:

$$\delta_H = 1 - 14,3 \cdot \left(1 - \nu - 2\nu^2\right)\frac{HV}{E},$$

where HV is the Vickers hardness of the material, E is the Young's modulus, and ν is the Poisson's ratio of the material.

When studying nanohardness, it is necessary to eliminate the influence of the scale factor, determining the hardness not at a constant load, but at a constant value of the hardness impression [3].

By the length of microcracks in the corners of the microhardness print, the fracture toughness of the material is determined. In the lower temperature range, the fracture stress and even the Weibull parameter m can be determined [4].

Thus, the indentation method, in opposed to the standard methods for determining mechanical properties, makes it possible to study the features of the dislocation deformation mechanism for brittle under standard mechanical tests RC and to obtain a complex of mechanical properties of strength and plasticity. The same complex of mechanical properties can be obtained on coatings from the RC. The obtained mechanical properties, in particular, the plasticity characteristic δH, can be correlate with the electronic structure of the RC.

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GRAPHENE-LIKE d-TRANSITION METAL DICHALCOGENIDES, VAN DER WAALS NANOSTRUCTURES: FROM PAST TO FUTURE

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Presented review is devoted to research in the fields of chemistry, technologies, and materials science of layered d-Transition Metals Dichalcogenides which were fulfilled at Institute for Problems of Materials Science of NASU. These studies were initiated by Samsonov G.V. and Obolonchik V.A. in 1965: the main stages, achievements and results of the executed works are shown.

Now, interdisciplinary research on nanochemistry, nanotechnologies and controlled properties of graphene-like d-Transition Metals Dichalcogenides and van der Waals nanostructures are being carried out at the Institute for Problems of Materials Science of NASU for design of new 2D nanomaterials on their basis. In this connection, the current trends of these studies in the developments, priorities, main problems and possible solutions are discussed.

Semiconducting graphene-like d-Transistion Metal Dichalcogenides (2D TMD; $2H\text{-}MCh_2$, M=Mo, W, Re; Ch=S, Se; "ultrathin nanosheets"; "few-layers nanoparticles", "single layer") are inorganic structural analogues of graphene. Now 2D TMD nanosheets and their van der Waals nanostructures (2D/2D, including graphene; 2D/3D, 2D/1D, 2D/0D) are gaining large interest for many new applications (nanoelectonics, nanooptoelectronics, nanocatalysis, nanosensors, biomedical nanomaterials, energy storage, etc) and have remarkable structure- and surface-sensitive semiconducting properties. TMD nanosheets and their van der Waals nanostructures have emerged as a fascinating new class of 2D "high-tech" nanomaterials.

Based on literature data and own results following problems of 2D nanotechnologies are analyzing:

- structural and technological advantages of graphene-like TMDs and differences their physical properties in comparison with analogical characteristics of another 2D nanoparticles;
- current state of graphene-like TMD nanotechnologies development;
- present problems of structure-, surface-sensitive semiconducting 2D properties control;
- last results of structure-, surface-sensitive physical properties of graphene-like TMDs studies.

Various design strategies of graphene-like TMDs as new 2D nanomaterials are reviewed:
- band-gap engineering;
- defect control and pore texture tailoring;
- surface sensitization and functionalization;
- dimensionality properties tuning;
- 2D nanostructures engineering for active sites enhancing ("edge states");
- functional architecture 2D assembly;
- structure-, surface-sensitive semiconducting 2D properties tuning (doping, intercalation);
- p-n-nanoheterojunction construction on different van der Waals nanostructures: 2D/2D, including graphene; 2D/3D, 2D/1D, 2D/0D).

The nanochemistry of graphene-like TMDs, and van der Waals nanostructures combined with original technological strategies that allow tuning of their semiconducting properties make these 2D nanomaterials very attractive for understanding the fundamental principles of nanoscienses, as well as for developing highly efficient, and affordable new 2D nanomaterials for large-scale production.

POLYCOMPONENT INTERMETALLICS

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In recent years, the number of papers has sharply increased, in which the features of the structure and, accordingly, the properties of not only binary but also three-four-component as well as polycomponent compounds are studied in detail. Among the three-component systems can distinguish a group of so-called nanolaminates (so called MAX-phases), which have a layered structure and low shear resistance at the basal plane, which provides a unique combination of properties of strength, heat resistance with a low temperature ductility. Some features of the temperature dependence of the strength characteristics of Ti_3SiC_2, Ti_4AlN_3, and Ti_3AlC_2 are considered.

It is well established that high levels of heat resistance of intermetallides such as Ni_3Al, Ti_3Al, and $TiAl$ are due to the peculiarities of the motion of superdislocations in such structures. The alloying of such binary compounds allows a significant change in the structure of such phases. Among the intermetallic phases, attention is drawn to the transition from binary compounds of the A_xB_y type to compositions when other elements can be located on the A and B sites. So, for example, when Ti_3Al is doped with zirconium and silicon, a compound $(Ti, Zr)_3 (Al, Si)$ appears. It is of interest to form high-entropy intermetallides, when in a system of 5-6 or more elements.

Some regularities in the formation of σ-, μ-phases, Laves phases [2] are established. The Laves phase is formed if two elements have a radii difference of more than 15% and a greater heat of mixing. To form the μ phase, a difference in the stoichiometry of two groups with different radii of 3: 1 is necessary, for example, $(Fe,Co,Ni)_3 (Mo, W)$. The σ-phases arise at an electron concentration of 6.7 -7.2 eV / atom and consist of so-called sigma-forming elements (Fe,Cr,Mn, Mo,Co,Ni,V).

A characteristic features of polycomponent (highly entropic) alloys and phases are the high entropy of the mixture and the presence of severe distortions associated with the

displacement of essentially all atoms from the ideal sites of the crystal lattice.

It can be argued that for this reason the thermodynamic stability of such phases with increasing entropy will decrease and, in the limit, we can proceed either to solid solutions or even to amorphization of such systems.

It can also be expected that a decrease in the degree of order that is unavoidable with such an alloying can lead to an increase in the plasticity of such phases and, possibly, an increase in the ductility of alloys strengthened by multicomponent intermetallic phases. Some loss of heat resistance of the phases with such doping can be compensated for by an abnormally high solid-solution hardening in a highly entropic metal matrix and the heat resistance of the alloy as a whole can turn out to be quite high. This path seems promising for the development of a new generation of heat-resistant materials. A promising direction is to obtain unusual two-dimensional intermetallides based on MAX-phases and a large group of layered materials.

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REFRACTORY COMPOUNDS AND COATINGS BASED ON HIGH-ENTROPIC ALLOYS

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The appearance of a new class of metal multicomponent high entropic refractory compounds caused their extremely poor knowledge, and the potentially promising operational properties of such materials and coatings open up wide opportunities for their research.

The work is devoted to the study of the properties of high-entropic oxides, carbides and nitrides based on various metals.

Coatings were obtained by vacuum arc method and ion sputtering in a plasma of a compressed discharge.

The initial materials for the production of coatings were high entropy alloys (HEA) with a hardness in the region of 3.4-7.2 GPa.

It is shown that when depositing in high-entropy alloys in vacuum or argon, the coatings basically retained their phase composition. The hardness of such coatings varied between 6.5-19.0 GPa, depending on the composition of the target.

The effect of sputtering regimes on the structure and physico-mechanical characteristics of magnetron coatings is shown.

Nitride high-entropy coatings obtained by the vacuum-arc method with a constant negative potential on the substrate and nitrogen pressure from 0.27 to 0.66 Pa had high hardness values of the order of 50-60 GPa and a contact modulus of elasticity of 320-400 GPa.

It was found that the coatings obtained in a compressed-discharge plasma possessed lower hardness values of the order of 42-52 GPa, but there is no drip component in the coating structure.

Electron-microscopic studies of these coatings were carried out. Their cluster structure is shown. Despite the considerable dispersion in the chemical composition, the calculated average atomic radius differs by no more than 2% at the analysis points.

High-entropic carbide coatings were obtained for the first time both in cast and in coating form. Cast high-entropic carbides were obtained by fusing various carbides. Coatings were obtained by spraying a cast high-entropy alloy in an arc discharge plasma in a mixture of argon and C2H2.

The hardness characteristics of high-enthalpy carbides are in the range 42-48 GPa, the contact modulus of elasticity is 270-330 GPa. The dependence of the physico-mechanical properties of the highly entropic carbide coating on the composition of the mixture

Oxide high-entropy coatings are obtained and investigated. Coatings were obtained by spraying a cast high-entropy alloy in an arc discharge plasma in a mixture of argon and oxygen at an operating pressure of ~ 0.5 Pa. The oxide high-entropy coatings are characterized by hardness at the level of 23-28 GPa, the contact modulus of elasticity is 210-230 GPa. Annealing of oxide high-entropy coating in air at 1100 $^{\circ}$C-5 h. led to a slight decrease in hardness to 17 GPa.

The wear resistance of the obtained coatings in a diamond-highly entropy coating pair was investigated. It is shown that the coefficient of friction for oxide and nitride coatings is at the level of 0.05-0.09. For carbide coatings, it increases to 0.12-0.15. The greatest spread was recorded for vacuum coatings. Depending on the composition, it varies from 0.15 to 0.45.

PROPERTIES OPTIMIZATION FOR n-ZnO AND p-NiO FILMS DEPOSITED BY MAGNETRON AND ION-BEAM SPUTTERING METHODS

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Transparent electronic devices (TED) typically use p-n junction and field effect transistor based on transparent oxide semiconductors (TOSs). TEDs have attracted considerable attention due to their great potential application in display technology, ultraviolet optoelectronics and energy conversion [1]. The high optical transparency in the visible range, low defect concentration and simple process of TOSs deposition are very important for designing high performance of TEDs. Therefore, it is of great interest to study the influence of deposition technology on the optical and electrical properties of TOS films as material of p-n junction that is the key unit of TEDs. ZnO is a one of the most widely used n-type TOSs for creation the p-n junction, due to its elemental abundance, large direct band gap and many deposition technologies. p-type NiO as a promising TOS with optical band gap of 3.4 eV have been chosen to form the p-n junction with ZnO TOS. Furthermore, only one stable phase in binary Ni-O system exists, allowing single phase NiO thin films to be easily fabricated. Therefore, the development of technology for deposition of quality n-ZnO and p-NiO films as TSOs materials for TEDs designing is very important and actual task of present materials science.

The reactive ion-beam sputtering (RIBS) and magnetron sputtering (MS) were utilized for the growth of n-ZnO and p-NiO films. RIBS and MS were considered to be the most interesting growth methods due to a good films adhesion, high deposition rates, film uniformity of over large substrate areas and easy control over the composition of the deposited films. Therefore, our report devoted to the optimization of technologies for growth of conductive n-ZnO and p-NiO films deposited by RIBS and MS.

The influence of technological parameters for MS and RIBS deposition methods on the structure, morphology, optical and electrical properties of ZnO and NiO films deposited on Si and glass wafers will be analyzed and discussed. The main conclusions are the following: (i) ZnO films, deposited in oxygen-rich conditions, demonstrate p-type conductivity, which however was not stable over time. (ii) The best film quality of conductive ZnO thin films was observed in the samples deposited by RIBS at substrate temperature of 200-250 °C and accelerating voltage of 6 keV. (iii) It has been shown that reducing the pressure of oxygen in the deposition chamber and increasing the substrate temperature, magnetron power and argon pressure leads to an improvement of the quality of p-type NiO films deposited by MS.

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TOPICS 1 (A)

Electronic structure and properties of refractory compounds

ELECTRONIC STRUCTURE OF Tl_4HgI_6 AS EVIDENCED FROM FIRST-PRINCIPLES BAND-STRUCTURE CALCULATIONS

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Halides with a common formula Tl_4BX_6 (were B – Cd, Hg, Pb; X – Cl, Br, I) belong to attractive series of compounds possessing wide transparency windows ranging from visible to far-IR regions. These halides are very promising materials for application in nonlinear optical devices, ionizing radiation detectors, sensors for temperature measurements, ion-selective electrodes.

The crystal structure of Tl_4HgI_6 is a task of controversy. Earlier, tetragonal space groups, centrosymmetric $P4/mnc$ and non-centrosymmetric $P4_2bc$, are considered to be a suitable approach for describing the crystal structure of the Tl_4HgI_6 compound. However, recent studies of stoichiometric Tl_4HgI_6 halide [1] have revealed that it crystallizes in space group $P4nc$ with unit cell parameters a=0.9416(3) nm and c=0.9237(5) nm.

In the present work we have performed band-structure calculations of Tl_4HgI_6 dealing with two kinds for exchange-correlation potential, namely generalized gradient approximation by Perdew-Burke-Ernzerhof (PBE), and modified Becke-Johnson (MBJ) exchange potential. In addition, the GGA+U technique is used as well as spin-orbit (SO) coupling effects are taken into account in order to consider relativistic effects. Our results indicate that the best agreement with the experimental X-ray photoelectron spectroscopy (XPS) data is achieved when calculations are made within MBJ+U+SO technique. Our results indicate that the upper and central portions of the valence band of Tl_4HgI_6 are dominated by contributions of the I 5p states, while the main contributors to its bottom are the Tl 6s and Hg 6s states.
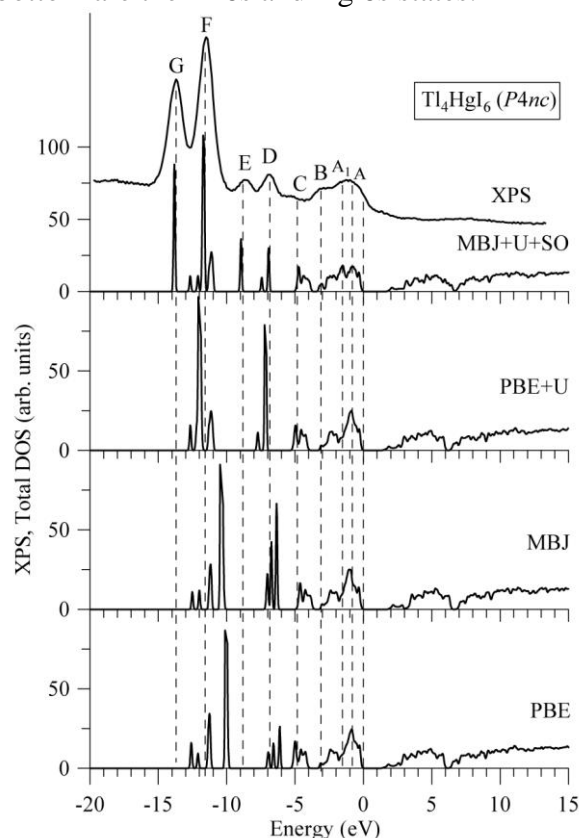
Fig. 1. **DFT calculations of total densities of states made in different approaches for exchange-correlation potential.**

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AB INITIO THERMODYNAMICS OF 2H-MoS$_2$ WITH DENSITY FUNCTIONAL PERTURBATION THEORY

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Hexagonal layered molybdenum disulfide 2H-MoS$_2$ is currently at the forefront of technology, because of its individual nanostructures, semiconducting electronic properties, and prospects in nanocomposites. Thus, reliable values of its thermodynamic properties, as well as understanding of specific inputs into them, are of crucial technological importance.In the recent decade density functional theory (DFT) became a widespread tool for quantum-chemical calculations of solids. Currently it can reliably predict such technologically important properties as thermodynamic functions, but it is rarely used for this purpose.The aim of this work is to calculate the low temperature heat capacity and standard values of thermodynamic properties of 2H-MoS$_2$ and compare them with reliable experimental data.

Calculations were done using *Quantum Espresso* package with local density approximation (LDA)for exchange-correlation potential (it was shown to give better results for structures with Van-der-Vaals bonding[1]). To compute enthalpy of formation and study the influence on its value of structure relaxation total energy calculations were done for three experimental and relaxed structures: bcc Mo, orthorhombic S, and 2H-MoS$_2$. Integrations over the Brillouin zone for each structure were done using Monkhorst-Pack meshes888, 822, and 882 respectively. Phonon spectrum and density of states (DOS) were calculated for molybdenum disulfide only. Heat capacity was calculated by integration of the phonon DOSconsideringstatistical distribution of phonons by energies. Standard values of enthalpy, entropy, and enthalpy of formation were calculated using classical thermodynamic relations.

Results of the heat capacity calculation are shown on fig. 1 together with literature data from [2]and demonstrate good agreement with the latter up to around 240 K. Deviation of the two sets at higher temperatures are, probably, an accumulation of experimental errors and thermal expansion input.
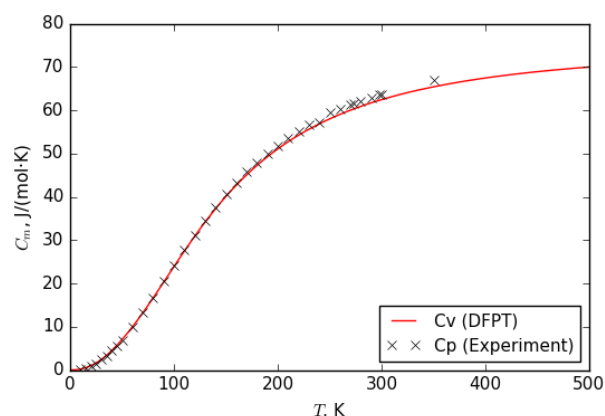
Fig. 1–Heat capacity of 2H-MoS$_2$

Values of thermodynamic functions at 298 K are given in table , with literature data from [2] for comparison, and they also demonstrate good agreement, considering that thermal expansion input is not included.

Table. 1 Thermodynamic functions of 2H-MoS$_2$ at 298,15 K

Function	$\Delta_f H$, kJ/mol	C_p, J/(mol K)	S, J/(mol K)	$H(T) - H(0K)$, kJ/mol
Calculation	274,6 (Exp.) 280,7 (Relax.)	61,95	61,63	10,33
Experiment	275±5	63,55	62,74	10,58

Enthalpy of formation calculated from experimental cell geometry agrees with literature better than from the relaxed cell, although both values are almost within experimental error.

Good agreement between the calculation results and literature demonstrates reliability of DFT for quantitative prediction of thermodynamic properties.

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PHYSICO-MECHANICAL PROPERTIES OF COMPOSITESBASED ON REFRACTORY NITRIDES SINTERED AT HIGH PRESSURE

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Superhard composite materials based on cubic boron nitride are widely used in cutting tools. Most of these materials have a microcrystalline structure. Recently, interest in nanocrystalline materials has increased in connection with the possibility of increasing their physico-mechanical characteristics. At present, the properties and conditions for obtaining superhard composite materials based on cubic boron nitride with a nanocrystalline microstructure have not been studied insufficiently.

The purpose of this work was to investigate the density and hardness of Q composite based on silicon and titanium nitrides with an oxide binder [1], with the addition of cubic boron nitride cBN of different granularity, depending on the sintering temperature in the 1200 - 1800 ° C range at a pressure of 5 GPa. Nano- and submicron cubic boron nitride powders were used in an amount of 50 wt. % as components of the initial charge. Sintering was performed in a modernized high-pressure apparatus of the "anvil type with hollows" on DO137A press unit with a force of 5 MN. The Vickers and Knoop hardness was determined at 10 N load. Fig. 1 shows the results of measuring the properties of the composite as a function of the sintering temperature and the dispersion of cBN powder.

It was found that the Q-cBN composite with the addition of nanocrystalline cubic boron nitride possesses the highest hardness. At the same time, the optimal sintering temperature is approximately 250 ° C lower than when submicron cubic boron nitride powder is used.

As a result of the research, a new superhard nanostructured material "Belanit", having a Knoop hardness of 26.1-27.6GPa, Vickers 42.5-46.5 GPa with a density of 3.40 g/cm^3 and Young modulus up to 535 GPawas obtained. It is promising for use in a metal-cutting tool. The technology of manufacturing plates with soldered elements from

the developed superhard Q-cBN(nano) material has been developed (Fig. 2).
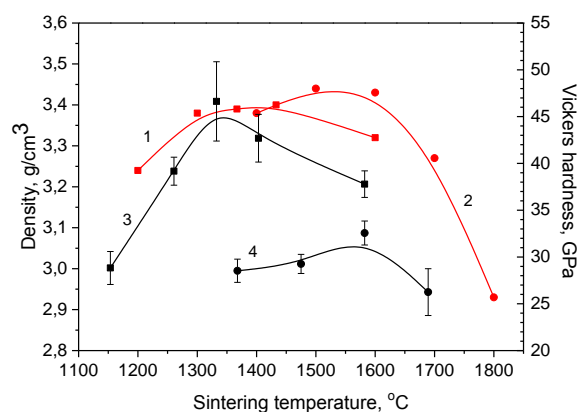
Fig. 1, Dependence of the density (1,2) and the Vickers hardness (3,4) of the composite on the sintering temperature and the dispersion of the initial cBN powder: 1, 3 –50% cBN(nano), 2.4 – 50% cBN(submicro).
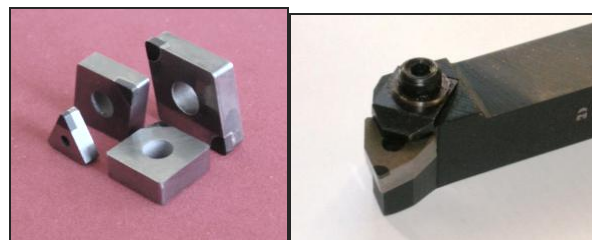
Fig.1. Multifaceted carbide plates with soldered cutting elements from "Belanit" and the type of cutter with mechanical fastening.

Reference

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POLYGONIZATION IN THE STRUCTURE OF WELDED JOINTS OF STEAM PIPELINES

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The metal of welded joints of steam pipelines (steel 15Х1М1Ф, 12Х1МФ), more than 270000 hours, operated for a long time under conditions of creep Te = 545 °C, Pe = 25 MPa is gradually weakened. More than the main metal.

Dislocations in the initial structure of welded joints are dispersed randomly and, in the course of their operating time, can partially annihilate, and partially in motion with a certain redistribution, form by deformation the wall of dislocations of the same sign. Such walls are located perpendicular to the effective sliding plane, are characterized by a relatively low energy and are represented as the boundaries of highly perfect subgrains with their insignificant orientation difference. The resulting structural state can be considered as a variant of the process of polygonization that takes place when the metal of welded joints is localized, which is 3-8%. In the presence of relatively small, with a mutual orientation, subgrain, when the hardness is reduced by about 10%, there is a narrowing of the x-ray lines. The polygonization of the metal of welded joints is characterized by a significant structural heterogeneity, which is formed when sliding and sliding the dislocations simultaneously. In the conditions of creep, sub-boundaries can form both existing dislocations and those that have arisen again. The formation of dislocation loops is facilitated by operating stresses. The displacement of the stress concentration in the α-phase crystals, which is caused by the displacement of dislocations, leads to the gradual formation of new loops throughout the crystal. After the formation of the first loops, their subsequent formation is accelerated. Sub-boundaries are mainly formed as a result of the redistribution of existing dislocations and by the displacement of the resulting (new) dislocations. The presence of formed sub-boundaries, in which dislocations are located at a close distance from each other, represents that dislocations creep from their glide planes. Confirmed by the position of Cotrella, that the disintegration of the strips of asterism into points, with a knit with the formation of walls from dislocations. Such a structural state is energetically more advantageous.

The motion of dislocations, as well as their redistribution, ensures the formation of various cells, whose mutual misorientation is insignificant. Sub-boundaries are represented as a set of parallel dislocations, the displacement of which occurs along the main slip system <III>. Polygonalization boundaries are perpendicular to the main slip plane. Areas between sub-boundaries represent subgrain or fragments. The polygonization boundaries consist mainly of edge dislocations. The formation of the polygonal structure depends on the speed of the dislocation creep, which is controlled by the energy of the package defects (the level of dislocation splitting), which is relatively low in the α-phase crystal. Segregation of chromium and molybdenum, elements of substitution, in the border zones of α-phase grains locally reduces the effect of polygonization. However, the manifestation of polygonization is more marked in the central zones of grains. Segregation of chromium and molybdenum in the border areas reduces the growth rate of subgrains. One subgrain of the two is formed, which is facilitated by the merging of their boundaries. Movement and partial elimination of grain boundaries are noted.

The study of polygonization features is useful for developing the concept of creating a new generation of heat-resisting and high-temperature steels.

ОПРЕДЕЛЕНИЕ ТВЕРДОСТИ АЛМАЗА С ПРИМЕНЕНИЕМ АТОМНО-СИЛОВОЙ МИКРОСКОПИИ И МИКРО-РАМАНОВСКОЙ СПЕКТРОСКОПИИ

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Атомно-силовая микроскопия (АСМ) применялась для получения 3D изображения отпечатка Виккерса на грани (111) синтетического алмаза типа Ib. Конфокальная рамановская спектроскопия и Kelvin probe force microscopy (KPFM) применялись для исследования структуры материала в отпечатке. Было установлено, что отпечаток Виккерса на поверхности алмаза не имеет резких и четких границ (Рис. А и В). Однако, применение АСМ в режиме фазового контраста выявило новую вязкоупругую фазу в отпечатке (Рис. С). Рамановская спектроскопия и KPFM показали, что новая фаза в отпечатке – это графит. Вероятно, что при внедрении индентора в алмаз образовывалась неизвестная фаза высокого давления углерода, которая при снижении давления превращалась в графит [1]. Площадь слоя графита в отпечатке на поверхности алмаза принималась нами за площадь контакта под нагрузкой и использовалась для определения твердости. Кроме того, определение твердости алмаза было выполнено с учетом упругой деформации алмазного индентора во время испытаний. Это дало нам возможность значительно повысить точность определения твердости алмаза. Было получено, что твердость по Виккерсу грани (111) синтетического алмаза типа Ib при нагрузке 5 Н равна 79,7 ГПа.
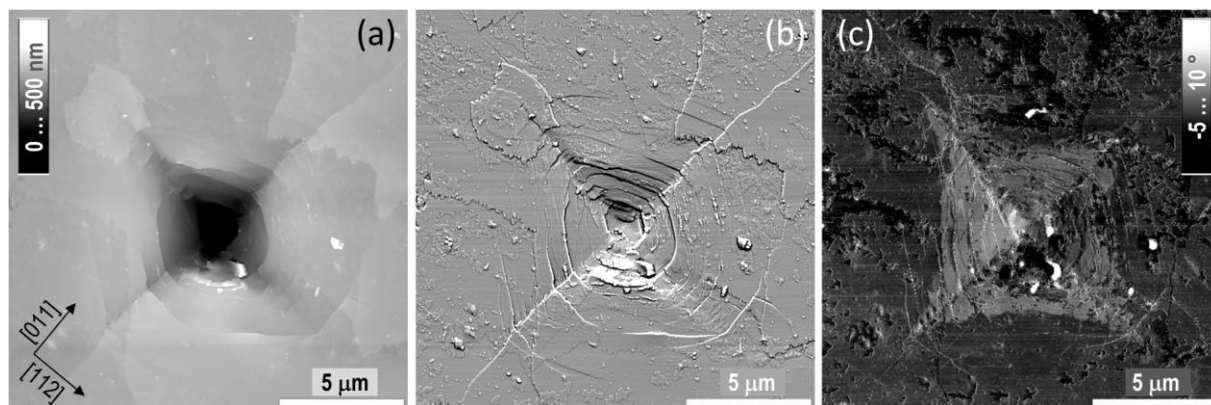
Рис. АСМ изображение отпечатка Виккерса на грани (111) синтетического алмаза. *a* – АСМ в режиме топографии поверхности, *b* – производная от рис. *a*, *c* – фазовый контраст.

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DENSITY OF ELECTRON STATES OF AMORPHOUS CoSi2

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Scientific research of physical properties of cobalt silicide is important for application of such materials in microelectronics and nanoelectronics. Cobalt silicide was used at production of super large scale integration circuit and definite elements of electronics [1, 2]. Popular method for production of electronic circuit is using thin films of metal silicides.

Such films are amorphous if metal silicide was deposed on non-heated substrate. Therefore it is necessary to know main features of the density of electron states of these materials.

The present thesis was devoted to research of the density of electron states $CoSi_2$. The density of electron states was calculated based on spectral dependences of optical constants of such material [3]. Theoretical equation from book by N.F. Mott and E.A. Davis [4] were used at our research. The method of our calculation was described in scientific paper [5]. It has been established that the valence band top of $CoSi_2$ is formed by d-electrons of Co in considerable part. These d-electrons provide essential contribution in the density of electron states conduction band together with 4s electrons of Co. Next p-electrons of Si provide contribution in the density of electron states $CoSi_2$ both at valence band and at conduction band.

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ATOMIC STRUCTURE OF AMORPHOUS SiCN

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Thin films of silicon nitride carbon (SiCN) are used as protective and wear-resistant films [1]. Amorphous SiCN has a stable structure and high oxidation resistance at temperatures above 1500°C [2]. SiCN films are promising for microelectronics and coatings.

Simulation of the amorphous atomic structure of $Si_{43}C_{43}N_{42}$ was carried out with the help of the first-principle quantum molecular dynamics from the program package "Quantum ESPRESSO" [3]. For calculating the interaction between electrons and ions, Vanderbilt's ultra-soft pseudopotentials were used.

The figure shows partial pair correlation functions of the resulting amorphous structure.
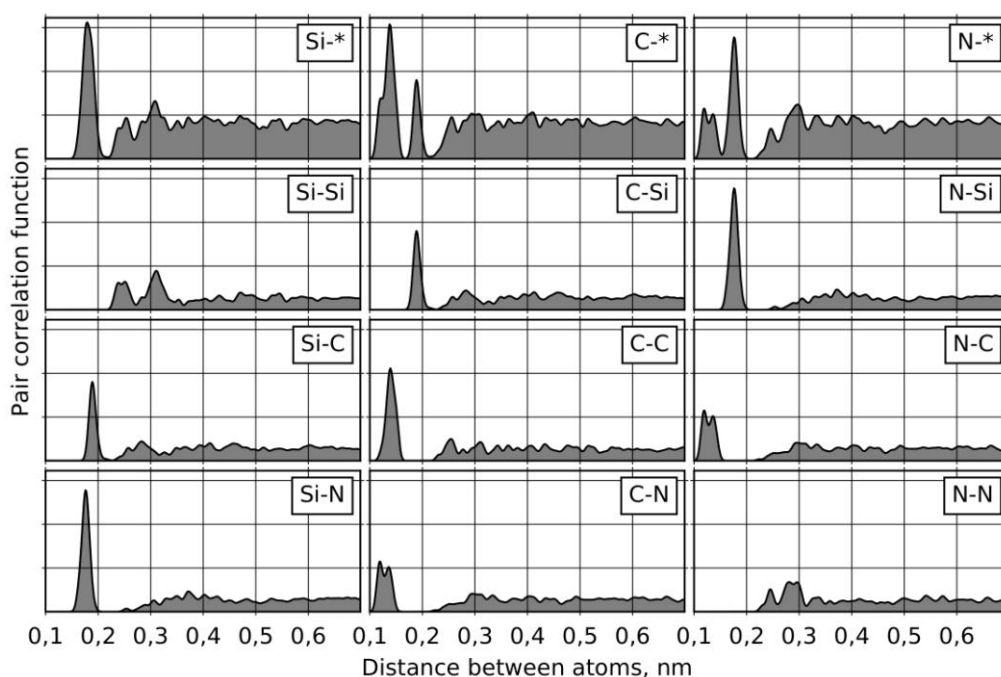
It can be seen that in the immediate environment of the atoms Si and N there are no identical atoms. In the case of the Si atom, this can be explained by the fact that the atomic radius of such an atom is much larger than the radii of atoms C and N. With regard to the absence of N atoms in the closest environment of N atoms, it can be linked with a stronger interaction of N atoms with Si and C atoms as compared to the interaction of N atoms with each other.

In the immediate vicinity of Si atoms, the number of N atoms is much larger than the number of C atoms. A similar picture is observed in the case of the closest environment of atoms N, where the Si atoms are much larger than the C atoms. Such a grouping can be related to the formation of stronger ties between the Si and N atoms compared with the Si-C and C-N bonds.

The most probable shortest distances between atoms, determined by the peaks of partial pair correlation functions, are: 0,127(C−N), 0,139(C−C), 0,176(Si−N), 0,189(Si−C), 0,245(Si−Si) та 0,245(N−N) nm. All distances except for the latter are somewhat smaller than the shortest interatomic distances in the corresponding crystals. Perhaps this reduction in the length of interatomic bonds is due to an increase in the multiplicity of these bonds.

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STABILITY PROPERTIES OF NBC-SIC ALLOYS FROM FIRST PRINCIPLES

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Solid solutions based on transition metal compounds (MX) are widely investigated due to their unique properties. They combine good mechanical, electrical and chemical properties and are used in industry. However, the stability of MX-SiC solid solutions (alloys) is studied incompletely. In this work, first-principles calculations were carried out to investigatethe stability of $B1-Si_xNb_{1-x}C$ solid solutions, since these alloys were not studied at all.

To study $Si_xNb_{1-x}C$ (x=0, 0.25, 0,5, 0.75 and 1.0) solid solutions we considered the 64-atom supercell of $Si_nNb_{32-n}C_{32}$, n = 0, 8, 16, 24, 32. All the compositions were generated using the SQS algorithm [1].

Scalar-relativistic band structure calculations within the density function theory (DFT) were carried out using the Quantum-ESPRESSOcode [2]. First-principles calculations were performed using periodic boundary conditions and the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [3] for the exchange-correlation energy and potential. Vanderbilt ultra-soft pseudo-potentials were used to describe the electron-ion interaction [4]. We performedthe relaxation of the initial $B1-Si_nNb_{32-n}C_{32}$ structures in order to find the lattice parameters and mixing energies for each composition. Results (not shown here) indicate that the lattice parameter and mixing energy have positive deviation from Vegard's law. This fact usually indicates towards phase separation.
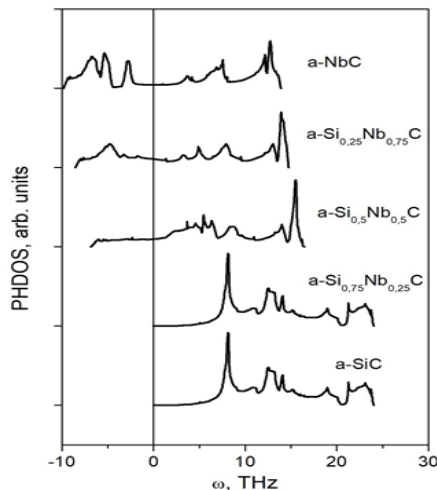
Fig. 1. Calculated phonon density of states (PHDOS) for B1-SiC for different lattice parameters (a) that correspond to those in $Si_xNb_{1-x}C$ solid solutions.

Phonon density of states (PHDOS) was calculated for each composition. The results (not shown here) point to the presence of the imaginary frequencies in the phonon spectra of the alloys for intermediate compositions. This usually means that the alloys are dynamical instable. Also, we calculated PHDOS for B1-SiC with lattice parameters that were equal to those of the alloys. The results are shown in Fig. 1. For the lattice parameters that correspond to the alloy compositions with x=0.5, 0.25 and 0.0, PHDOS of B1-SiC hasthe range with imaginary frequencies. It follows that the main role in the instability of the solid solutions plays the dynamical instability of B1-SiC with large lattice parameters.

Elastic properties of solid solutions were also investigated. Figure 2 shows the calculated bulk modulus (B), shear modulus (G) and Young modulus (E) as functions of composition. One can see that the elastic moduli of the alloys are lower compared to those of B1-NbC and B1-SiC. The modulus B determined from the elastic constants for x=0.75 has a negative value (-542.23). It is well known that a structure will be stable provided all the eigenvalues of the stiffness matrix will be positive. For x=0.75, we found that one of eigenvalues is negative and thus, $Si_{0.75}Nb_{0.25}C$ should be unstable.
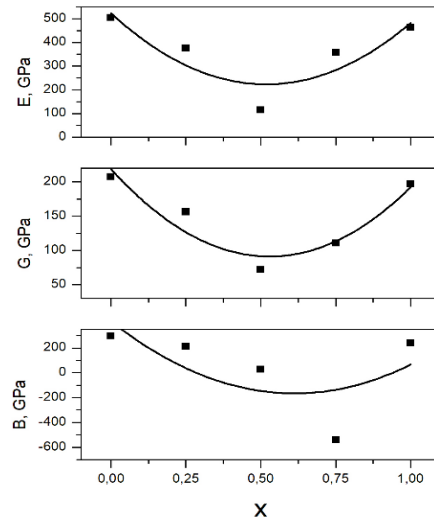
Fig. 2. Calculated bulk modulus (B), shear modulus (G) and elastic modulus (E) for $Si_xNb_{1-x}C$ as functions of composition x. Solid lines are the result of parabolic interpolation of the calculated points.

PHDOS for B1-NbC-SiC solid solutions has imaginary frequencies and therefore solid solutions would be dynamically unstable. Also, this conclusion is confirmed by the results of the calculations of elastic properties that show that stiffness matrix has negative eigenvalues.

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CRYSTALLIZATION OF THE SYSTEM Ru-Rh-Ir ALLOYS

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A study of the ternary Ru–Rh–Ir system was undertaken in connection with the research of phase equilibria in quarternary systems of the IV group transition metals with refractory Platinum group metals. This system is the basis for the quarternary systems Hf(Ti, Zr)–Pn–Pn'–Pn'', namely, the Hf–Ru–Rh–Ir, for which the two boundary ternary systems phase diagrams were constructed by us earlier [1, 2].

Alloys of hafnium with these metals, besides scientific interest, are perspective from the point of view of their possible application as heat-resistant structural materials, catalysts, hydrogen adsorbents, in semiconductor technology [3]. Alloys based on $HfRh_3$ and $HfIr_3$ compounds ($CuAu_3$-type), called «refractory superalloys», are proposed for use as coatings of gas turbine details [4].

The ternary Ru–Rh–Ir system is studied for the first time. Alloys were prepared from components in an electric arc furnace with a nonconsumable tungsten electrode in a gettered argon atmosphere. To select the temperature of homogenizing annealing, alloys in as-cast state were studied by differential thermal analysis. The melting temperatures of the alloys were determined by the Pirani-Altertum method on cast and homogenizing samples. Annealing of the alloys was carried out at subsolidus temperatures (20—30 °C below the melting point). The as-cast and annealed alloys were investigated by differential thermal, microstructural (by light optical microscopy), X-ray diffraction and microprobe analyses.

As a result of the study we obtained experimental data about phase equilibria character at subsolidus temperatures and studied the processes of crystallization of alloys. On the basis of these data the melting diagram of the ternary Ru–Rh–Ir system was plotted. Ternary compounds are not found in the system.

It was found that in the Ru–Rh–Ir system at subsolidus temperatures a wide region of a ruthenium-based solid solution exists. It extends deep from the ruthenium angle of the concentration triangle into the ternary system up to 49 at.% Ir and 60 at.% Rh in the corresponding binary systems Ru–Ir and Ru–Rh. Also a wide range of a continuous series of solid solutions between isostructural components rhodium and iridium takes place. The maximum extent of it containing 45 at.% Ru is reached in the binary Ru–Ir system. The width of the two-phase region (<Ru> + <Rh, Ir>) in the ternary system does not exceed 6 at.%.

The incongruent process L + <Ir> ↔ <Ru> taking place by monovariant curve outgoing from the boundary Ru–Ir system at 2395°C, up to finish at 2090°C in the Ru–Rh system changes character twice (L ↔ <Ru> + <Rh, Ir>, L + <Ru> ↔ <Rh, Ir>).

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APRIORITY PROGNOSING OF IMPURITIES INFLUENCE ON PROPERTY OF ALUMINIUM PHASES, CONTAINED THE TRANSITION METALS

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It is known, that phase stability of envier materials always is a function from atomic and electronic parameters. In most cases perspective materials with highe temperature properties concludes aluminium or compounds with one.

However, it's recognized, the stability property this phases as – *Fe₃A*l, *Cr₃Al*, *Ni₃(Ti, Al)*, *Ni₃Nb*, quickly decreases when in atomic structure arises noncontroling impurities.

<u>This report</u> was discussed the combined approach of estimates mutual solubility of elements in structure aluminium phases with transition metals. It is to be noted, Samsonv's principe was oriented to search of driving force for a phase transitions. Decision of this problem ought to the complex investigates whith quantum-mechanical calculations of an interatomical energetical processes and the electronic-charge ordering by Habbard or other model.

Nowadays it may be done in a frame of the combined approaches with non-spinpolarised Hedin-Lundquist's (tabl.1) method and by the Quality Atomicisomorphical Substitution Theory [1, 2].

<u>Table 1</u>. Change number of valent *s-*, *p-*, *d-*electrons by charge transfer from *Al* to atoms *Ni*.

Phase	Q_sNi	Q_pNi	Q_dNi	Q_sAl	Q_pAl	Q_dAl
Ni	0,63	0,70	8,60	–	–	–
Ni₃Al	0,65	0,79	8,70	0,90	1,15	0,35
Al	–	–	–	1,13	1,43	0,40

The analyses by versions $\pm\Delta E_n/E_n$ gives change <u>electron-tendency.</u> The structural <u>load creep</u> prognosing by $\pm$ $\Delta K_e/K_e$ potential (fig.1). **Conclusion:** This approach give rise to regulation material science effects, <u>optimization *cost value*</u> technology, <u>to yield increase of market prices</u> on *innovations goods*.
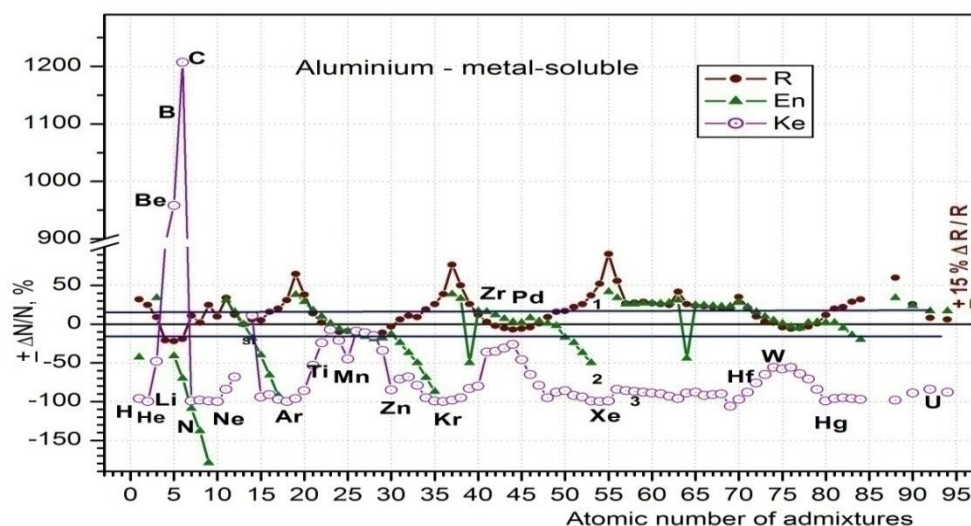
Fig. 1. Certification Card *CC*II «*Many alloing (impurities) elements – the only metal–soluble* » for analyzing direction charge transfer and driving force for fase transitions: parameter $\pm\Delta R/R$~ δ local defects area; electronegativity $\pm\Delta E_n/E_n$~ μ chemfactor; energodynamical $\pm\Delta K_e/K_e$ coefficient of load creep[1, 2].

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THE APRIORITY QUICK–FORECASTING OF THE NONCONTROLLING ADMIXTURE INFLUENCE ON PROPERTIES OF THE HIGH ENTHROPY MATERIALS BY MEANS POWDER TECHNOLOGY

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It is know, that aluminides and silicides are wery valuable phases for auto-, instrumental, constructive materials productions. But, techno-logy raw, as a rule, have many of alien and strange chemical elements (admixtures). If follow to the Samson`s principles of prognosing for stability of high temperature properties of phases, it needs to estimate distinctions for atomic and electronical parameters between components and admixtures.

This <u>report dealt with</u> *method of apriority forecasting* by special the *Certifications Cards* (*CC*1, fig.1) of possibility mutual influence on nonsolubility and property in structures of a high enthropy materials from the pouder technology.On the *CC*I are repesented for aluminium *Al*, silicon *Si*, phosphorus *P*, sulphur *S* atoms curves: $\Delta\Omega/\Omega$ % – percent distinctions to atomic volumes, $\Delta S/S$ – shortest interatomis distances, $\Delta\Sigma_m/\Sigma_m$ – high-energy atomic parameter, $\Delta K_e/K_e$ – energodyna-mical potential of atomical structure, $\Delta E_n/E_n$ – electronegativity, which ~ μ chemical potential.

Application of this method *gives* <u>«key»</u> for <u>understand</u> of the phase transformation *mecha-nism*; this <u>give rise to optimization technology</u> as a whole and helps regulation *cost value* of materials as *a innovations goods*.

Conclusion: The Certifications Cards (CC1) *«One a soluble element – multitude a changeable metal-solvents»* allow to do quik-forecast of useful elementary composition for new high enthropy materials from the pouder technology.

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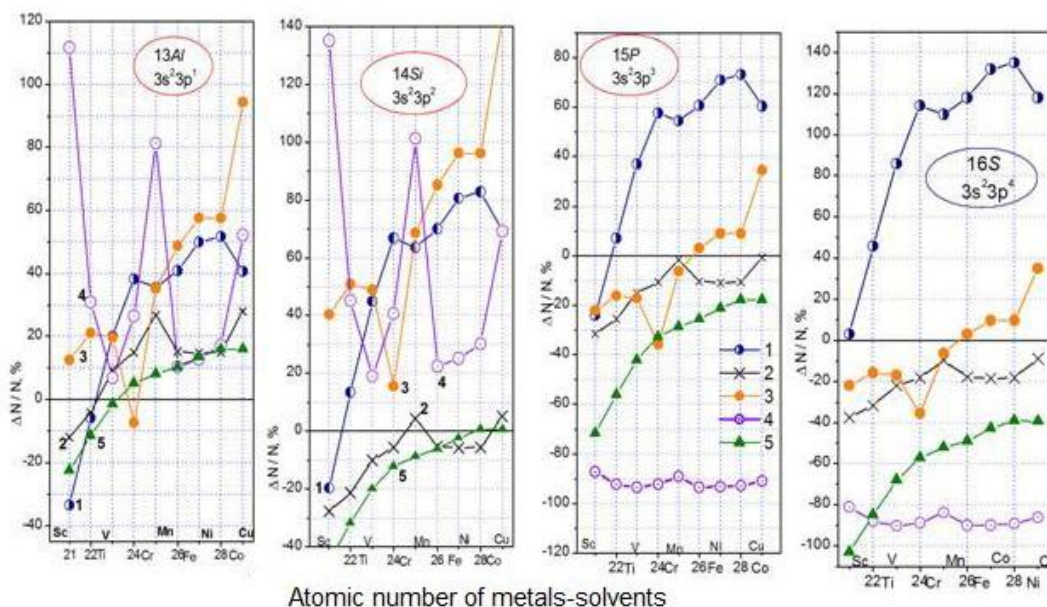
Fig. 1. Certification Card *CC*I «*One a soluble element – multitude a chageable metal–solvents* » for the estimate of the phisico-chemical influence admixtures on the defects of a sublatices into structure of the highentrophy materials:

1 – $\Delta\Omega/\Omega$, %; 2 – $\Delta S/S$, %; 3 – $\Delta\Sigma_m/\Sigma_m$, %; 4 – $\Delta K_e/K_e$, %; 5 – $\Delta E_n/E_n$

REGARD TO MARTENSITIC TRANSFORMATION IN QUENCHED ALLOYS OF Hf-Nb SYSTEM

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Alloys based on transition metals of the IV and V groups of the periodic system of elements, with the possible occurrence of martensitic transformation (MT), are promising trend in the field of the physics of functional materials. The melting point of the alloys of the Hf-Nb system, which lies within the range of 2065 to 2469 °C, makes it possible to relate this group of alloys to refractory compounds.

The Hf-Nb and Ti-Nb systems have a similar kind of state diagrams, in addition, hafnium possesses physical and chemical properties similar to titanium and zirconium. In turn, Ti-Nb and Zr-Nb systems are already well studied, in the alloys of these systems, the MT occurrence and the presence of functional characteristics are detected. Thus, it can be assumed that in the Hf-Nb system, martensite-type phase transformation and the presence of functional properties, such as superelasticity and shape memory effect, are possible. Alloys of the Hf-Nb system may be interesting in the development of functional alloys with high temperature shape memory effect (SME) and the development of medical supplies alloys since they possess a high degree of biocompatibility. Unlike titanium and zirconium, hafnium has an electronic f-shell, which leads to higher temperatures of allotropic transformation. Temperatures of quenching, depending on the chemical composition, lie in the range of 1300-1700 °C. This, in turn, makes it difficult to carry out experiments. Literature sources of information on the presence of MT in the alloys of the Hf-Nb system have not been found, so the question about existence of the martensitic transformation in alloys of this system is topical.

Analyzing the phase diagrams of the Ti-Nb and Zr-Nb systems, as well as the MT temperature intervals in these alloys, it can be assumed that in the Hf-Nb system phase transformation of the martensitic type exists at concentrations of niobium up to 30 at. %, therefore for research were selected $Hf_{100-x}Nb_x$ alloys, where x =15, 20, 25, 50.

Analysis of the quenched alloy $Hf_{50}Nb_{50}$ revealed the presence of a bcc structure (β-phase), and separation of α-Hf. Functional properties not found.

Снижение концентрации ниобия до 25 ат. % Nb led to a radical change in the structure, there was formation of a clearly marked acicular structure typical for the martensitic phase (Figure 1). This alloy showed the presence of the shape memory effect, MT temperatures lie in the range of 90-300 °C.

For alloys $Hf_{80}Nb_{20}$ and $Hf_{850}Nb_{15}$, apparently, it was not possible to reach the required quenching temperature, since the microstructure of these samples is similar to the not completely recrystallized structure. MT and functional properties are not detected.
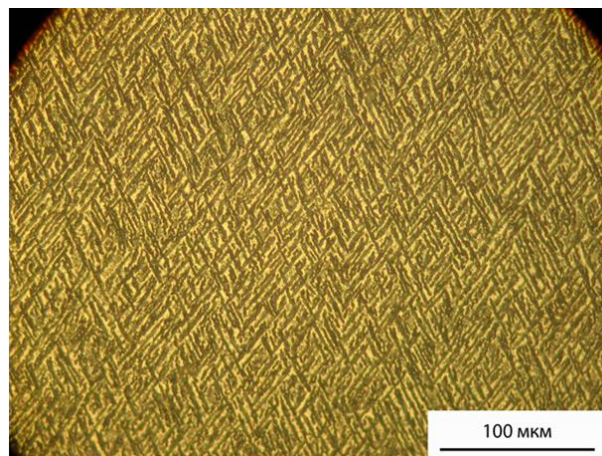
Fig. 1. Microstructure of the quenched $Hf_{75}Nb_{25}$ alloy.

PHASE RELATIONS IN THE La_2O_3-Er_2O_3 (Yb_2O_3) SYSTEMS

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System with lanthana and erbia are perspective for the development of transparent ceramics, laser and other optoelectronic components, ceramics for the intermediate temperature solid oxide fuel cells with high ionic conductivity.

The objective of this work is to investigate the phase relations in the binary La_2O_3-Er_2O_3 (Yb_2O_3) systems at 1100 to 1600 °C in air in the whole concentration range. Lanthanum oxide, La_2O_3, erbium oxide, Er_2O_3 (all 99.99% produced by Merck Corp.) and analytical grade nitric acid were used as the starting materials. The lantania and erbia powders were preliminary dried at 200°C for 20h followed by dissolving in hot diluted nitric acid (1:1). The La_2O_3−Er_2O_3 (Yb_2O_3) samples were prepared in concentrationstep of 1–5mol% from nitrate solutions with their subsequent evaporation and decomposition at 800°C for 2h.

The X-ray analysis of the samples was performed by powder method using DRON-3 at room temperature (CuKα radiation) with step size of 0.05–0.1 degrees in the range $2\theta = 15$–$90°$. Lattice parameters were refined by the least squares fitting using the LATTIC code. The accuracy in the lattice parameter of cubic phases was within 0.0002 nm.

The study of solid state reaction of La_2O_3 and Er_2O_3 (Yb_2O_3) at temperature 1100 - 1600 °C showed that three types of solid solutions based on hexagonal modification of A-La_2O_3, cubic modification of C-Ln_2O_3 and intermediate phase with perovskite-type structure of $LaErO_3$, $LaYbO_3$ (R) with rhombic distortions in the La_2O_3-Er_2O_3 (Yb_2O_3) systems are formed. These solid solutions were separated with the two-phase fields: (A + R) and (C + R). The boundaries of the homogeneity fields for the solid solutions based on A-La_2O_3, C-Er_2O_3 and $LaErO_3$, $LaYbO_3$ as well as lattice parameters for solid solutions were determined.

The refined solubility of Er_2O_3 in A-modification of La_2O_3 is about 5 mol % at 1100 °C (9820 h) and is about 13 mol % at 1500 °C (225 h). The lattice parameter of the unit cell varies from $a = 0.6523$ nm, $c = 0.3855$ nm in pure $La(OH)_3$ to $a = 0.6504$ nm, $c = 0.3828$ nm in the sample containing 95 mol % La_2O_3-5 mol % Er_2O_3 at 1100 °C (9820 h) and to $a = 0.6477$nm, $c = 0.3815$ nm in the sample containing 85 mol % La_2O_3-15 mol % Er_2O_3 at 1500 °C (225 h). It has been found that the boundaries of the R-phase homogeneity field in the concentration range of 45-51 mol % Er_2O_3 at 1100 °C (9820 h) and at 1500 °C (225 h). The lattice parameters of the unit cell R phase varies from $a = 0.6056$, $b = 0.5843$, $c = 0.8442$ nm in single-phase sample, containing 50 mol % La_2O_3-50 mol % Er_2O_3 to $a = 0.6064$, $b = 0.5859$, $c = 0.8453$ nm in two-phase sample (R + C), containing 49 mol % La_2O_3-51 mol % Er_2O_3 and to $a = 0.6071$, $b = 0.5855$, $c = 0.8454$ in two-phase sample (A + R), containing 55 mol % La_2O_3-45 mol % Er_2O_3 at 1100 °C (9820 h) and to $a = 0.6060$, $b = 0.5856$, $c = 0.8416$ nm in two-phase sample (R + C) containing 48 mol. % La_2O_3-52 ml. % Er_2O_3 and to $a = 0.6068$, $b = 0.5862$, $c = 0.8442$ in two-phase sample (A*+ R), containing 55 mol. % La_2O_3-45 ml. % Er_2O_3 at 1500 °C (225 h).

The refined solubility of La_2O_3 in C-modification of Yb_2O_3 is about ~2 мол. % at 1100, 1500 i 1600 °C. The lattice parameter of the unit cell varies from $a = 1,0432$ nm in pure Yb_2O_3 to $a = 1,0446$ nm at 1100 °C (13316 h), $a = 1,0453$ nm at 1500 °C (50 h), $a = 1,0441$ nm at 1600 °C (10 h)

The refined for the boundary solid solution.solubility of Yb_2O_3 in A- modification of La_2O_3 of about 4 мол. % at 1100 °C and ~9 мол. % at 1500 i 1600 °C. The lattice parameter of the unit cell varies from $a = 0,6523$ nm, $c = 0,3855$ nm in pure $La(OH)_3$ to $a = 0,6557$ nm, $c = 0,3864$ nm 8453 in two-phase sample (A + R), containing 55 mol. % La_2O_3 – 45 mol. % Yb_2O_3 (1500 °C)

INDENTATION SIZE EFFECT OF HARDNESS OF REFRACTORY COMPOUNDS

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Hardness is one of the methods for determining the mechanical properties of materials and depends from the indent size and, consequently, from the applied load. As a rule, when the load on the indenter decreases, the hardness values of crystalline materials increases. This effect is especially expressed during determination of nanohardness and is known as the indentation size effect of hardness.

The authors suggest to determine the hardness value H at the standard (depth-fixed h) depth of the indent or to recalculate the hardness to this standard depth for eliminate the indentation size effect of hardness.

For determination the hardness value H_f at depth-fixed size of indent h_f, the next equation may be used [1]:

$$H_f = H \left(\frac{h_f}{h} \right)^{m-2}.$$

There H is the hardness at displacement of indenter h. Constant m could be determined as $m = d \log P / d \log h$, if the hardness was measured at different loads P. The constant m can also be approximately determined from the single loading curve in the coordinates $P - h$, from the power dependence $P = const \cdot h^m$. Authors propose to use h_f equal to 100 nm for high-hardness materials.

Determinination of the hardness value at a fixed size of indent but not at a fixed load P, allows to exclude the indentation size effect of hardness. This approach also allows to compare more accurately the mechanical properties of materials.

The values of nanohardness at $h = h_f$ obtained by the authors for the refractory compaunds are given in the table.

In this work, theoretical calculation of the dependence of hardness H from the depth of the indent h for some refractory compounds was made on the basis of the above mentioned equation and the data of the table (see Fig. 1).

Table. The values of displacement of indenter h_{max}, nanohardness H at the given maximum load on indenter P, Young's modulus E, constant m and recalculated nanohardness H_f at fixed displacement of the indenter h_f.

Material	P_{max}, mN	E, GPa	h_{max}, nm	H, GPa	m	H_f at $h_f = 100$ nm
BeO*	10	400	181.5	12.8	1.58	**16.5**
TiN°	50	440	394.3	24.6	1.72	**36.2**
Si₃N₄**	50	324	415.3	24.3	1.67	**39.0**
NbC*	50	550	359.3	31.3	1.65	**48.9**
ZrN*	50	400	400.7	24.3	1.65	**39.7**
TiB₂**	50	540	308.2	44.1	1.63	**66.7**
WC*	50	700	310.6	39.8	1.59	**63.6**
LaB₆*	50	439	336.6	38.7	1.53	**68.0**
ZrC**	50	480	386.0	26.4	1.63	**43.3**
B₄C°	10	500	123.3	48.9	1.64	**52.8**
Al₂O₃*	10	409	144.9	33.3	1.64	**38.0**

* – Single crystal, ** – Polycrystalline, ° – Individual grain.
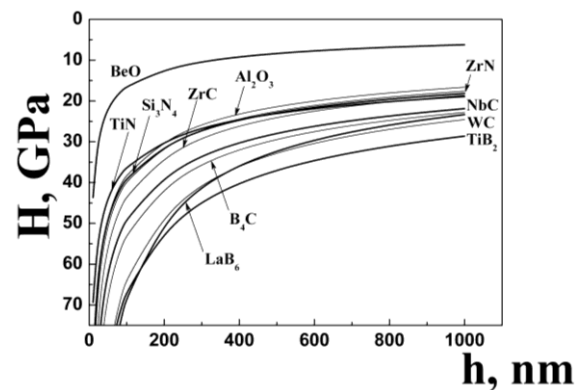
Fig. 1. The dependence of calculated hardness H from the depth of hardness indent h for some refractory compounds

The results of the calculation of $H(h)$ show that the indentation size effect of nanohardness is very important for refractory compounds.

The method of measuring the hardness at the same (fixed) depth of the indent h_f allow to exclude the indentation size effect of hardness and makes it possible to compare the results of the measurement of nanohardness obtained in different studies.

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PLASTICITY OF REFRACTORY COMPOUNDS
IN A WIDE TEMPERATURE RANGE

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The plasticity characteristic, determined by indentation method δ_H by the value of microhardness, was introduced by the authors in [1]. The value of δ_H is determined by the equation given below or more precisely for superhard materials in accordance with the formulas of [2]:

$$\delta_H = 1 - 14{,}3 \cdot \left(1 - \nu - 2\nu^2\right)\frac{HV}{E},$$

where HV is the hardness of the material indented by the Vickers indentor, E is the Young's modulus, and ν is the Poisson's ratio of the material.

The introduction of this characteristic made it possible to determine and compare the plasticity of materials with different types of interatomic bonds and different crystal structures. The use of this characteristic is especially important for materials that break brittle under standard mechanical tests. These materials include refractory compounds, which can be studied by the hardness method in a wide range of temperatures, including cryogenic and elevated to 1000 °C using a diamond indenter and up to 1350 °C with the use of a sapphire indenter.

We have studied $\delta_H(T)$ for NbC, ZrC, WC, SiC, Al_2O_3, B_4C, $B_4C+40\%ZrB_2$ (Fig.1). At cryogenic temperatures, the test was carried out on a PMTN unit under a coolant layer, and at high temperatures in a vacuum at a modernized VIM-1 unit. It can be seen from Fig. 1 that δ_H at room temperature for all the studied refractory compounds is lower than 0.9, which indicates that they break brittle under standard mechanical tests.

For particularly brittle materials (SiC), an athermal section is observed on the H(T) curve at low temperatures. Our investigations show that in the region of sharp H(T) dependence the main mechanism for the formation of a hardness impression is plastic deformation and here one can use the notion of δ_H.
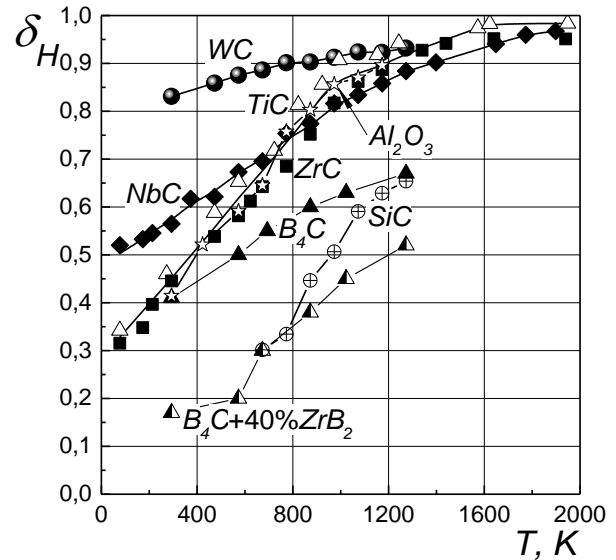
Fig.1. Temperature dependence of the plasticity characteristic δ_H of refractory compounds.

At the athermal section of H(T), the main mechanism is brittle fracture, and here we should use the concepts of fracture physics.

WC, as can be seen from Fig. 1, at all the studied temperatures has δ_H higher than δ_H for NbC and ZrC. Probably, that's why WC works well in WC-Co hard alloy, and WC substitution on NbC or ZrC is not effective, although the hardness of NbC and ZrC is higher than that of WC.

This example shows that the study of the hardness of refractory compounds should always be accompanied by the calculation of δ_H, since the mechanical behavior of the materials is most thoroughly defined by both the strength characteristics and the characteristics of their plasticity.

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STRUCTURE AND PROPERTIES OF PROFILED TUNGSTEN SINGLE-CRYSTALS PRODUCED BY METHOD OF PLASMA-INDUCTION GROWING

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E. O. Paton Electric Welding Institute of the NAS of Ukraine has developed a technology and equipment for layer-by-layer plasma-induction growing of single-crystals of refractory metals, which allow producing coarse profiled single-crystals [1]. However, the problem of increase of efficiency of the process of plasma-induction growing with preservation of single-crystalline properties of received ingots is still relevant. Aim of the present work is evaluation of the effect of rate of plasma-induction growing on structural perfection of tungsten single-crystals.

Single-crystal tungsten ingots were produced using six modes at different rates of the process from 17 to 70 mm/min. Five layers were built up at each mode, except for mode with maximum rate (70 mm/min) which contained three layers. Examination of structure (microhardness, subgrain structure size, subgrain-boundary angles, nature of dislocation distribution etc.) was carried out at all structural levels using a complex of experimental methods of modern physical metallurgy, including optical metallography (Neophot-32 and Versamet-2, Japan; Leco-M400, USA), analytical scanning electron microscopy (SEM) (Philips SEM-515, Netherlands) as well as transmission selected-area diffraction electron microscopy (JEM-200CX, JEOL company with accelerating voltage 200 kV, Japan). The fine foils for transmission microscopy was prepared using two-step method, namely preliminary electro-polishing with further multiple ion thining by argon flows in specially designed unit.

Examinations of structure of tungsten single-crystal oriented on plane (110) show that thickness of build up layers (on 20 μm edge) makes 2-3 mm; structure of layers is uniform, no defects and pores are observed. Metal microhardness insignificantly reduces from 4290-4400 MPa to 4010 – 4200 MPa at transfer from minimum rates (17 mm/min) to maximum rates (70 mm/min) with decrease of subgrain size from 20-32 μm to 15-25 μm.

Transmission diffraction examinations of the fine structure determined that at minimum rates a distribution of dislocations in single-crystal volume is uniform at their density $(2\dots4) \times 10^{6}$ cm^{-2}. At transfer to the maximum rates dislocation density rises by order at uniform its distribution in metal volume (without rapid gradients). Dislocation structure nature is uniform, i.e. dislocation rings have well-defined relief, different sign dislocations are well-seen that indicates their annihilation.

The most significant criterion, i.e. evaluation of grain-boundary angles of substricture on procedure [2] was used for estimation of structural perfection received at different modes of growing of single-crystal ingot. It is shown that the mode with maximum rate of build up results in insignificant refinement (1.3 times) of substructure at uniform (gradient-free) distribution of dislocation density and production of tungsten single-crystals with perfect single-crystal structure (low-angle boundary) at grain-boundary angles do not exceeding 3 °. At that the maximum build up rate allows significant reduction of time of ingot production. It is determined that the structural factors, providing under service conditions crack resistance of profiled tungsten single-crystals is uniform dislocation distribution and absence of extended dislocation accumulations, i.e. concentrators of internal stresses.

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INVESTIGATION OF THE STRUCTURE AND PROPERTIES OF EUTECTIC Nb-Mo-B ALLOYS

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The system Nb-Mo-B is of great interest in terms of developing new high-temperature materials and heat-resistant coatings.

In our previous works [1-3] we investigated Nb-Mo-B alloys at temperatures of melting-solidification and, basing on experimental data, constructed the solidus and liquidus surface projections, phase diagram at melting (solidification) and reaction scheme. The aim of the present work was investigated structure and mechanical properties of eutectic Nb-Mo-B alloys.

The alloys of 7 compositions were prepared by melting in an electric arc furnace from pure constituents in Ar. Cast alloys were studied by X-ray diffraction analysis and metallography (scanning electron microscopy and EPMA).

The microhardness of the phases and structural constituents in the cast samples was measured on the PMT-3 device at room temperature at loads of 0.196, 0.49 or 0.98 N, and the duration of the exposure was 15 seconds. For each phase were made 5-10 measurements. The hardness of alloys from room temperature up to 900 °C (hot hardness) was determined in vacuum of 10^{-3} Pa by static injection of an indenter from a sapphire at a load of 9.81 N (exposure was 60 sec). Before measurement the sample was kept at a given temperature for 3-5 minutes.

With the increase of the content of molybdenum the microhardness of the bcc matrix and the eutectic of the metal-boride Nb-Mo-B alloys increases (Table 1). In the obtained alloys there are highly dispersed eutectics $Nb_{1-x}Mo_xB_y + (Nb_{1-x}Mo_x)_3B_2$, $Nb_{1-x}Mo_xB_y + (Nb_{1-x}Mo_x)_3B_2 + (Mo_2B)$ i $(Mo) + (Mo_2B)$ with high content boride phases, which increases with increasing molybdenum content. Their microhardness 10−12; 15.6 and 16.9 GPa, respectively. As shown that the concentration dependences of the microhardness of the boride phases $(Nb_{1-x}Mo_x)_3B_2$ and $(Nb_{1-x}Mo_x)B$ demonstrated a maximum at a commensurable content of metals, ~ 50 and ~ 62 GPa, respectively. The temperature of the incipient of sharp softening of the base alloy $Nb_{81.8}B_{18.2}$ was obtained to be is high, ~680 °C. As obtained the three-component alloys $Nb_{60.6}Mo_{20.2}B_{19.2}$ and $Nb_{39.9}Mo_{39.9}B_{20.2}$ are characterized by high hardness, 5.1−9.1 GPa.

Table. 1. Microhardness of phases and eutectics of cast Nb-Mo-B alloys

Alloy, % (at.)	Microhardness, $H\mu$, GPa		
	matrix	eutectic	boride
$Nb_{81.8}B_{18.2}$	—	3.67	42.9
$Nb_{60.6}Mo_{20.2}B_{19.2}$	7.13	9.41	36.3
$Nb_{39.9}Mo_{39.9}B_{20.2}$	7.83	12.6	62.3
$Nb_{15.7}Mo_{62.9}B_{21.4}$	—	15.6	—
$Nb_{7.8}Mo_{70.5}B_{21.7}$	—	16.9	—
$Nb_{15.4}Mo_{39.6}B_{45}$	—	—	42.9
	—	—	50.7
$Nb_{25}Mo_{25}B_{50}$	—	—	58.8

So, the alloys of investigated system in the metal-boride ranges have high ambient-temperature microhardness and hardness at elevated temperature and are promising for applications as high-temperature materials and heat-resistant coatings.

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MECHANICAL PROPERTIES OF COMPOSITE MATERIAL OF Ti-TiB SYSTEM BY BLENDED ELEMENTAL POWDER METALLURGY ON THE BASIS OF TITANIUM HYDRIDE

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One of the most effective technologies of obtaining sintered materials on the basis of recently developed titanium alloys is the use as a raw material of titanium hydride powders instead of serial titanium powder, which provides intensification of diffusion processes during sintering, as well as the possibility of purifying interphase boundaries at the expense of atomic hydrogen released during the decomposition of titanium hydride..The efficiency of using titanium hydride as the main component component for the production of titanium based metal-matrix composites using traditional powder metallurgy methods is shown. The most promising results from the point of view of providing microstructural homogeneity and reduction of residual porosity were achieved for titanium composites reinforced with TiO particles obtained by sintering TiH_2 powder mixtures and TiB_2 titanium diboride [1]. In this paper the basic mechanical properties of metal-matrix composites of the Ti / TiB system with different content of the reinforcing component are investigated. It was shown that their porosity plays a decisive role in the mechanical properties of composite materials, so it is 1.5% for samples without boride inclusions, up to 7.5% for presses sintered from a charge of 10% from TiB2. The values of tensile strength, hardness and elastic modulus, despite some porosity growth of the sintered alloy, increase with the introduction of 5% of TiB2 powder into the composition of the charge, while increasing the content of the high modulus component in the charge to 10% leads to a decrease in the level of these characteristics. The plasticity of the sintered alloys monotonically decreases with increasing content of the boride component (Fig. 1).
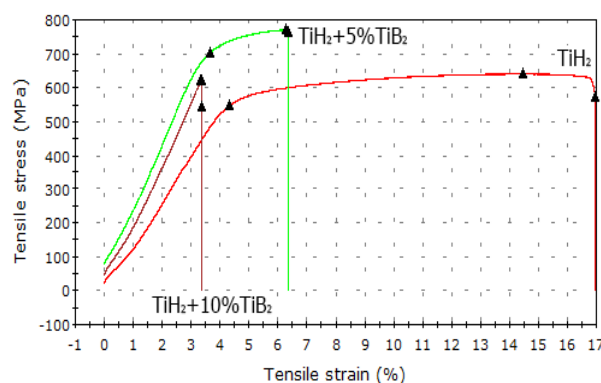
Figure 1. Stress-strain curves for titanium MMC

However, in a compression test, the value of the boundary of proportionality and the boundary of plasticity increases monotonously with increasing content of the boride component, despite increasing porosity of materials.

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STRUCTURE AND PROPERTIES OF LaB$_6$-TiB$_2$-Cu COMPOSITE OBTAINED BY SPARK PLASMA SINTERING

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Spot welding is the most effective technique of joining metal parts in the production of cars, household appliances, medical equipment, and others. The most loaded node at spot welding is a tip - an electrode. Traditional materials of such electrodes are copper heat-resistant alloys (bronze). Proceeding from the main requirements of the materials of the electrodes, namely: the ability to maintain the initial shape, size and properties when heated to a temperature of 600 ° C (and above) and resistance to shock forces (~ 5 kg/mm^2), which is significantly shorten the life of the work and/or reduce the quality of the treated surface. A promising direction for the development of effective contact for point welding is the production of materials by powder metallurgy, which are an electrically conductive matrix (usually Cu) reinforced by fine particles of a refractory compound (W, WC, Al$_2$O$_3$, etc.). One of the problems for such contacts is that as the content of conductive metal increases, the contact resistance decreases, as well as the resistance to erosion, which entails a number of problems, is deteriorating. In the opposite case, when the content of the refractory compound increases - the wear of the contact decreases, but the electrical conductivity drops sharply (more than three times). Such unwanted processes occur due to the fundamental difference between the matrix and the dispersed inclusions. Therefore, the purpose of the work is to create new heterophases composites with conductive matrix (Cu), penetrated by a refractory frame (LaB$_6$-TiB$_2$). It should be noted,

that the refractory frame of LaB$_6$-TiB$_2$ is formed from particles of a composite with eutectic structure (LaB$_6$ matrix reinforced by single crystal TiB$_2$ fibers with diameter 0.1-0.3 μm). The use of the LaB$_6$-TiB$_2$ composite, as a refractory frame is due to high values of strength, hardness and electrical conductivity.

To achieve the goal, a mixture of (LaB$_6$-TiB$_2$) and Cu powders, with a refractory compound content of 70 vol%, was sintered at a temperature of 850 °C-1100 °C by spark plasma sintering method. Microstructure studies shown, that with increasing sintering temperature, residual porosity is reduced and continuous fused copper and refractory compounds are formed. Measuring the compressive strength showed that the composites sintered above 1000 °C are destroyed plastically and have strength of about 350 MPa. It has been established that the metal-ceramic composite has an electric resistance (1.09-5.76 μΩ·cm) at the level of traditional copper-doped electrodes doped with zirconium, nickel or chromium. The Rockwell hardness composites sintered at 1000 °C-1100 °C temperatures, reaching 80-85 HRB. On the basis of the analysis of the properties of the metal-ceramic composite (LaB$_6$-TiB$_2$)-Cu we can concluded that these materials will be able efficiently work as contact welding electrodes. To determine the location of the material in the range of electrodes it is necessary to measure strength at temperatures of 20 °C -800 °C, as well as natural tests for erosion resistance.

EFFECT OF THE STRUCTURE OF GRAIN BOUNDARIES ON THE PHYSICO-MECHANICAL PROPERTIES OF (LaB$_6$-TiB$_2$) -Cu COMPOSITES

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The metal-ceramic composites, due to the combination of properties of ceramic and metal materials, have high performance characteristics: hardness, wear resistance, durability, electrical conductivity, etc. However, the presence of a partition boundary between the ceramic and metal components of composite, which is characterized by a high degree of defects, is quite often cause a dramatically decrease in the physical and mechanical characteristics of metal-ceramics. One of the most effective methods of improving the strength of the material is reinforcement. Usually reinforcement provides the strength of the material by placing the reinforcing component in its volume of another component. The paper proposes a mechanism for increasing the physico-mechanical characteristics of a metal-ceramic composite (LaB$_6$-TiB$_2$)-Cu by reinforcing the boundary between the particles of the eutectic composition of LaB$_6$-TiB$_2$ and copper.

In order to obtain high-density (LaB$_6$-TiB$_2$)-Cu composites, the method of spark plasma sintering of powder mixtures was used. In order to obtain the structure of powder particles in "hedgehogs" modification of particles LaB$_6$-TiB$_2$ was carried out. The matrix phase was etched in nitrogen acid for receive bare TiB$_2$ fibers on the surface. The densification was carried out at temperatures of 850-1050 °C with a holding time of 2 min at maximum values. In order to save the initial structure of the surface of the LaB$_6$-TiB$_2$ particles and to ensure the reinforcement of the interface between the phases, a high heating rate of 200 °C/min and a minimum pressure (5 MPa) were used to pass the current through the set of the mold. The microstructure and phase composition of the sintered samples were investigated. The compression strength and electrical conductivity of the composites were also determined. The increase in the temperature of sintering is accompanied by a decrease in the initial porosity and the formation of strong contacts between the phases. Microstructure studies of the grain boundary of a composite, sintered at a temperature of 1050 °C (Fig. 1), indicate the formation of a reinforced grain boundary during densification of the powder mixture of the eutectic composition of LaB$_6$-TiB$_2$ and copper.
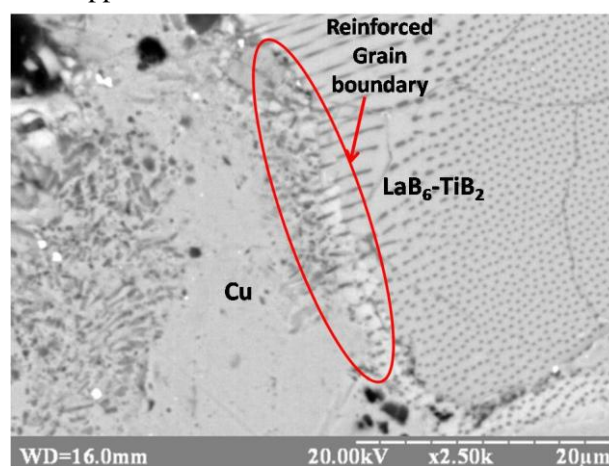
Fig. 1 - Microstructure of composite (LaB$_6$-TiB$_2$) - Cu with reinforced grain boundary

According to the results of X-ray diffraction analysis of sintered samples at 1000 °C and 1050 °C, the presence of additional phases: CuTi$_2$, LaBO$_3$, LaB$_3$O$_6$ was revealed, except for Cu, LaB$_6$ and TiB$_2$. Measuring the compressive strength showed that the composites with reinforced grain boundaries have strength of about 500 MPa. It should be noted that the strength of the composite with reinforced sections of the section is 25-30% higher compared with composites with non-reinforced grain boundaries. Measurement of the specific electrical resistance showed that it is at the level of 5-7 μΩ·cm.

Conclusions. The efficiency of reinforcing the grain boundaries of metal-ceramic composites (LaB$_6$-TiB$_2$)-Cu for increasing in strength is shown. This technique can be applied to other metal-ceramic systems.

TENSION IN THE MELTED ZIRCONIUM CARBIDE

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At present, the development of science and technology is largely facilitated by the use of solid refractory compounds, which include zirconium carbide. It can be used in the composition of high-temperature ceramics, structural materials in nuclear power engineering due to its low neutron absorption cross section ($Zr=1,37 \ 10^{-24}$, $C=1,3710^{-26}$) and other composite materials. Therefore, the study of its physico-mechanical properties, depending on its composition and method of obtaining, is an urgent task. At the same time, the available data on its properties, measured on different samples, differ from each other [1].

It should be assumed that the most reliable results of the properties can be obtained on single-crystal samples. In the first approximation to such samples can be attributed samples of melted refractory compounds, which were used in this paper [2].

Due to the fact that the properties of the materials largely depend on the strained-deformed state of their crystal lattice, stresses in the carbide phases of fused carbide of zirconium were investigated in comparison with hot-pressed with using the results of determining the lattice parameters by the formula [2]:

$$\sigma_I = \left(\frac{\Delta a}{a} \right) \cdot E$$

where Δa difference between lattice periods (fig. 1); E – Young's modulus, GPa.
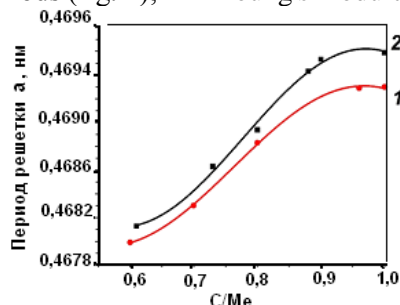
Figure 1 - Dependence of the lattice period of fused ZrC as a function of the carbon content in it (2) and by the data of [1] (1)

As can be seen from Fig. 1, the dependence of the lattice parameters on the carbon content to the materials obtained by different methods is the same. However, the values of the grating periods for carbide phases of fused carbide, other things being equal, are higher.

The calculated tension of the first type in the fused carbide phases vary in the range from 120 to 240 MPa, depending on the carbon content and the method of obtaining carbide. In the work on broadening of the diffraction peaks, we also determined the stresses of the second kind (β) (Fig. 2). The results corresponds to the data of [3].
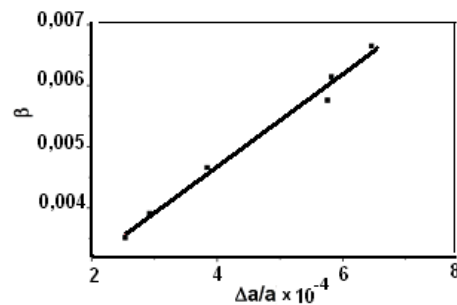
Figure 2 – Dependence tense I type (Δa/a) on microstresses II type (β)

Thus it was found that in ZrC carbide after its obtaining in a fused form, which can influence the formation of its physico-mechanical properties.

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ВЛИЯНИЕ Sr НА КРИСТАЛЛИЧЕСКУЮ СТРУКТУРУ КОМПОЗИТА BHA/GLASS

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Композиционные материалы на основе биогенного гидроксиапатита и стеклофазы (BHA/glass) широко используются для изготовления имплантатов костных тканей [1]. Имеются данные о положительном влиянии присутствия стронция в остеопластических материалах при определенном соотношении Ca/Sr [2, 3].

Sr вводился в количестве 1 %мас. в композиционный материал BHA/glass, с соотношением фаз 50/5% мас. Конечная термообработка проводилась при 780 °C и длительности 1 час.

Для исследования рентгенофазового анализа был использован рентгеновский дифрактометр ДРОН-3М, оборудованный дополнительной компьютерной системой сканирования, рентгеновской трубкой с медным анодом и никелевым фильтром. Таким образом, дифракционные картины были получены с помощью Cu-Kα излучения со средней длиной волны λ = 1,54178 Å3.

Вероятно, что введение стронция в BHA/glass приводит к уменьшению количества кристаллических фаз в сравнении с нелегированным композитом, а также способствует преобразованию кристаллической структуры композита за счет перехода кристаллических фаз в аморфную (рис. 1). А также, введение Sr приводит к изменению положения центров пиков BHA/glass и BHA/glass-Sr, снижению интенсивности пиков и смещения их в сторону больших углов у BHA/glass-Sr (рис. 2).
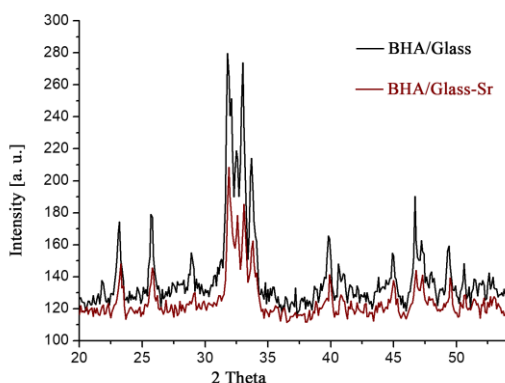
Рис.1. Дифракционная картина BHA/glass и BHA/glass-Sr.
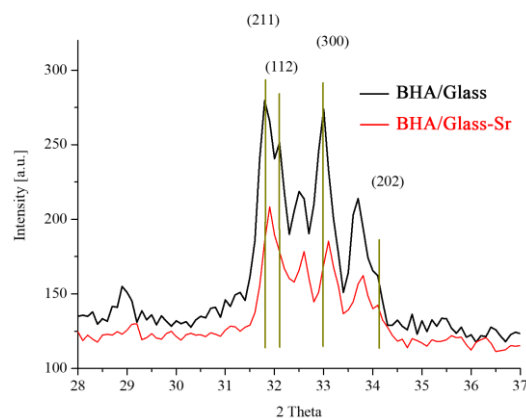
Рис.2. Дифракционная картина BHA/glass и BHA/glass-Sr для плоскостей (211), (112), (300), (202).

Выводы:

РФА показал, что полученные BHA/glass композиты являются гетерофазным материалом. Наличие стронция как легирующей добавки в композиционном материале BHA/glass оказывает влияние на соотношение фаз, а также приводит к изменению параметров элементарной ячейки BHA и кристаллической решетки гидроксиапатита.

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THERMODYNAMIC PROPERTIES OF ALLOYS
OF Ce-Sn AND Ce-Ni-Sn

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The purpose of the work is to investigate the thermochemical properties of the Ce-Sn melt at $0 < xSn$ 0.2 and Ce-Ni-Sn at 1600 -1800 K to five beam sections; Also, calculate the thermodynamic properties of these melts according to the IAS and Redlich-Kister models. We have identified and ΔH of the melts of the Ce-Sn system co-treated with literary data, also obtained by the method of calorimetry at 1890 K (Sudadtsova V.S. with co-authors). Our and literary data are jointly processed and the dependences and ΔH are obtained in the whole concentration range. It was shown that $=-267\pm12$, and $\Delta H_{min} = -67,0 \pm0,4$ kJ / mole at 1800 K and $x_{Sn} = 0.45$. This correlates with the behavior of these alloys in solid state. According to the diagram of the state of the Ce-Sn system, the Ce_5Sn_4 compound ($T_m. = 1780$ K, $\Delta_f H = -83.7$ kJ / mole) is refractory itself and that which is melted congruently. Using the own and literature thermochemical properties of the melts and intermediate phases of the Ce-Sn system, the thermodynamic properties of the melts and associates are calculated on the basis of the IAS model. As one would expect, the components of the components exhibit very large negative deviations from ideal solutions.

For alloys of the system Ce-Ni-Sn the phase equilibrium at $T = 670°C$ was investigated and the isothermal section was constructed (Skolozodra RV from 1988). According to this section, the components of this system form ~ 10 ternary intermetallics. As far as the thermodynamic properties of the limiting systems are concerned, they are investigated. The melt of all three limiting systems was formed with the release of heat. Therefore, we estimated $\square N$ melting of the ternary system Ce-Ni-Sn by the model of Redlich-Kister without and with a triple contribution $L_0 = -200$ and -400, respectively. As should be expected, the thermochemical properties of the Ce-Ni-Sn melts, calculated in this way, are different. To confirm which calculated ΔH correctly describe the nature of the data of the melts, we have identified them by calorimetry method at 1600-1800 K. The Ce-Ni-Sn melts installed and ΔH are shown in the figure. It can be seen that ΔH_{min} accounts for the compound Ce_5Sn_4. This means that the energy of the interaction of the melts of the ternary system Ce-Ni-Sn brings the binary subsystem of Ce-Sn. The comparison of experimentally determined ΔH from the calculations of the Redligh-Kister model without and with a triple contribution. Taking into account the relative errors of the definition of ΔH of melts (2-5%), we can conclude that the Redlich-Kister model with triple contribution $L_0 = -200$ best describes the enthalpy of mixing the melts of the Ce-Ni-Sn system. Taking this into account, we predicted the activity of the components, ΔG and ΔS melts on the same model. It was established that the activity of the components of the Ce-Ni-Sn melts exhibit very large negative deviations from ideal solutions, while $\Delta G_{min} = -42$ kJ / mol and $\Delta S = -12.8$ J / mole K also belong to the system Ce-Sn (Ce_5Sn_4), as well as for thermochemical properties.
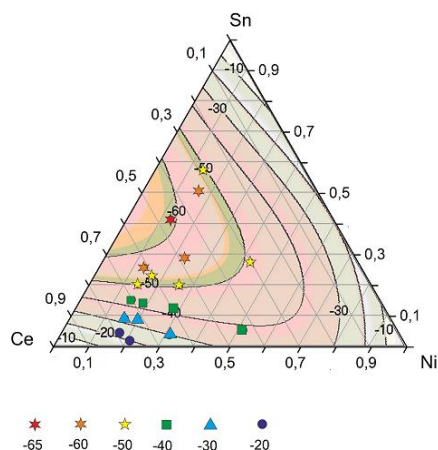
Figure. Isotenthalpy of mixing of melts ternary Ce-Ni-Sn system(points - experiment, lines - calculation)

TINTERACTION IN THE BINARY SYSTEM BaO-ZrO$_2$

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Refractory substances in the form of composites and mixtures are widely used in various branches of the national economy. The development of new refractory, ceramic, electroconductive materials requires knowledge of thermodynamic properties, diagrams of the state of systems and the mechanisms of their formation. In this paper, the transformations that occur when a mixture of the ZrO2-BaO system, taken in a 1: 1 weight ratio, are studied. The study of these mixtures was carried out on a derivatograph Q-1500 ° C with a heating rate of 15 K / min in a programmed regime.

It was established that the TG curve showed a decrease in mass with three jumps, and on the DTA curve three endo- and one exoeffect (table, figure). It is clear from the figure that the temperature intervals for the decrease in mass and heat absorption for the observed effects do not always coincide, although they are close. There are some differences with the literary data. The latter differences are caused by the unequal flow of processes, which is caused by heating the test mixture at a constant rate. All this must be taken into account when developing new materials with certain properties.

In addition, the cleaning of the surface of the particles of barium oxide from the adsorbed, crystalline hydrated water of barium carbonate makes it activated and capable of reacting with both air molecules and ZrO$_2$.

Using the standard enthalpies for the formation of reagents and reaction products, we calculated their thermal effects. As expected, they are all positive and vary from 250 to 350 kJ. This correlates with the areas of peaks recorded on the DTA curve.

Thus, the data obtained in the work are confirmed by the tarmodynamic calculations, in spite of the fact that the study of the mixture of the ZrO$_2$-BaO system is performed under nonequilibrium conditions. Hence, all the described transformations could be predicted using the tarmodynamic data for the substances under study and the data available in the literature for each reaction.

Somewhat unexpected is the exothermic process at 760-920 ° C, proceeding with mass loss. Most likely, in this temperature range BaCO$_3$ decomposes on the surface of BaO grains during its storage. In this case, barium oxide is formed in the activated state with very small grain sizes. In this form it is able to interact with zirconium oxide to form barium zirconate and release heat.

Table Decoding the DTA curve

Tempera-ture at our	interval (in ° C) in lit. given	Reaction
20-120		
120-210	125-130	Ba(OH)$_2$ · 8H$_2$O→Ba(OH)$_2$+H$_2$O
210-280		
310-420	408 до 500	Ba(OH)$_2$ = BaO+H$_2$O BaO+1/2O$_2$ = BaO
420-760		
760-920		2BaO$_2$ → 2BaO + O$_2$
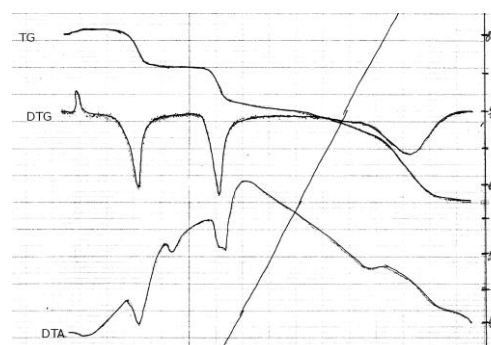
Drawing. Derivatogram of the ZrO$_2$-BaO system

TOPICS 2 (B)

Synthesis and sintering of composite materials based on refractory compounds and their properties

ALUMINUM DODECABORIDE- AND BORON CARBIDE-BASED CERAMICS

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The results of structural and mechanical properties study of hot pressed at 30 MPa, 1950 - 2240 ^{o}C and high pressure (2 GPa)-high temperature (1200-1400 ^{o}C) sintered and synthesized aluminum dodecaboride (a-AlB_{12}, $AlB_{12}C_2$, α-AlB_{12}-TiB_2-TiC)- and boron carbide (B_4C and B_4C-SiC)-based ceramics will be under the discussion. The materials can be used as protective armor or constructional ceramics for nuclear power plants, additives to the boron-carbide-based materials, as solid fuel, abrasives, explosives, etc. [1, 2]. The materials were manufactured from α-AlB_{12}, $AlB_{12}C_2$, C nanopowders and B_4C, SiC, TiC micropowders. The preliminarily mixtures of powders were prepared using high speed planetary activator.

The a-AlB_{12} powder without and with carbon additions can be sintered to the dense state at 1200-1400 ^{o}C, 2 GPa, 1 h, while hardness of the materials was not high (12.5-17.8 GPa at 49 N-load). The $AlB_{12}C_2$ nanopowder sintered at 1400 ^{o}C, 2 GPa, 1 h contained 89 wt.% $AlB_{12}C_2$ and 11 wt.% of admixture Al_2O_3 (according x-ray diffraction study) and demonstrated hardness H_V(49 N-load)=26.6±0.6 GPa, fracture toughness K_{1c} (49 N)=5.9±0.5 MPa·m$^{0.5}$, density γ=2.73 g/cm^3. The materials obtained at 30 MPa, 2240-1950°C had much higher characteristics. α-AlB_{12} (94-98 wt.%, p=2.53-2.58 g/cm^3) showed H_V(49 N)=24.1 GPa; K_{1c} (49 N)=4.9 MPa·m$^{0.5}$; bending R_{bs}=336 MPa and compressive R_{cs}=378 MPa strengths. Composite 74 wt.% $AlB_{12}C_2$, 22 wt% TiB_2 , 4 wt% Al_2O_3 (ρ=3.1 g/cm^3) had H_V(49N)=37.65±6.74 GPa, K_{1c}(49 N)=5.2 MPa·m$^{0.5}$, R_{bs} = 646 MPa and R_{cs} =795 MPa. B_4C(p=2.52 g/cm^3) demonstrated H_V(4.9 N)=40 GPa, K_{1c} (3-point bending)=4.89 MPa·m^{0,5}, R_{cs}=392 MPa, R_{cs}=1551 MPa and B_4C-20%SiC (p = 2.67 g/cm^3) had H_V(49 N)= 35 GPa, K_{1c}(3-point bending)=5.9 MPa·m^{0,5}, R_{bs}=474 MPa, R_{cs}=1878 MPa (Fig. 1).

Acknowledgements

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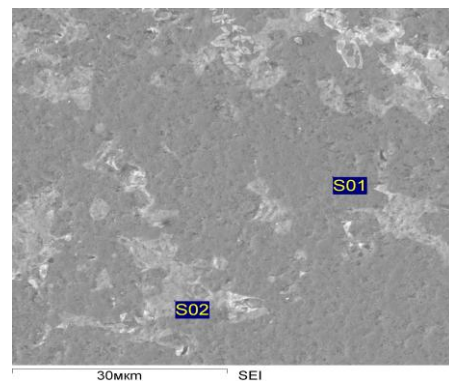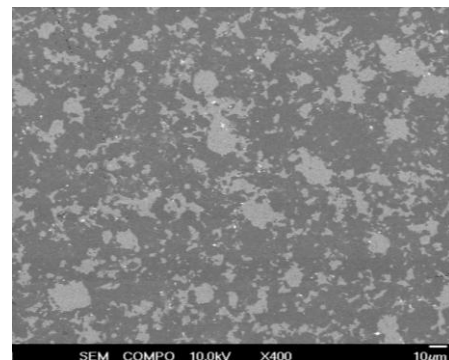
Atomic %

Spectrum	B	C	Si	Total
S01	78.3	21.5	0.2	100.0
S02		51.7	48.3	100.0

Fig. 1 Structure and composition of hot pressed B_4C-SiC based ceramics.

CORROSION RESISTANCE OF ZrB_2 BASED UHTC IN THE TEMPERATURE RANGE OF 1300-1500 ° C IN THE AIR

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A class of materials called ultra-high temperature ceramics (HfB_2) ZrB_2–SiC was identified as the most promising one for multiple space systems due to their melting point ($\geq$ 3000 °C) and high oxidation and ablation resistance as compared to SiC [1,2]. However, pure ZrB_2 or HfB_2monolithic ceramics, have a number of application limitations, such as poor compacting ability, critical corrosion resistance, and, therefore, the introduction of secondary phases is in need.

ZrB_2–15%$MoSi_2$material has been obtained according to the technology [1].

It is established that the obtained materials have a homogeneous structure with a zirconium diboride matrix. Molybdenum disilicide at the compaction process most likely interacts with zirconium and boron oxides (present as uncontrolled impurities) by the reactions [2]:

$$2MoSi_2 + 2B_2O_3 + ZrO_2 = \mathbf{ZrB_2} + 4SiO_2 + 2MoB$$
$$\Delta G^{273} = -318 \; kJ$$
$$2MoSi_2 + B_2O_3 + 2,5C = 2,5SiC + 1,5SiO_2$$
$$\Delta G^{273} = -270,4kJ$$
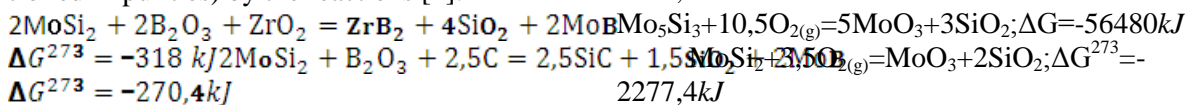
The lines of molybdenum boride, zirconium boride, residual molybdenum disilicide and solid solution on their base are detected by X-ray investigation. In the ZrB_2-MoB system, according to the [3], eutectic and solid solutions are formed. The presence of such interaction is confirmed by X-ray - ZrB_2 peak broadening and displacements.

The ceramics oxidation kinetics is shown in Figure 1. Parabolic oxidation curves at temperatures of 1300 and 1400 °C, and the logarithmic curve at 1500 °Cthere are observed.

By analyzing the X-ray diffraction spectrum, it can be seen that in the composite ZrB_2-15 vol.% $MoSi_2$the formation of the amorphous phase $(B_2O_3$-$SiO_2)$ is not observed [4], and there are only crystalline phases: m-ZrO_2, crystalline SiO_2, $ZrSiO_4$. The REM method has found that the thickness of the scale does not exceed ~ 15 microns, and consists a needle phase of $ZrSiO_4$ soaked by SiO_2, which increases the oxidation resistance in a given temperature range compared to [5].

The high corrosion resistance of the composite can be explained by the fact that molybdenum silicide contains up to 6% free silicon [6], and the process of interaction withoxygen
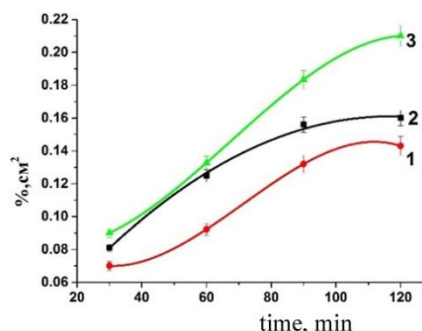
1– 1300 °C *2*–1400 °C *3*– 1500 °C

Figure1.ZrB_2 – 15% $MoSi_2$ ceramics oxidation kinetics.

occurs according to the most thermodynamically beneficial reactions:

$$5MoSi_2+7O_{2(g)}=Mo_5Si_3+7SiO;\Delta G^{273}=-5739,2kJ$$
$$Mo_5Si_3+10,5O_{2(g)}=5MoO_3+3SiO_2;\Delta G=-56480kJ$$
$$MoSi_2+3,5O_{2(g)}=MoO_3+2SiO_2;\Delta G^{273}=-2277,4kJ$$
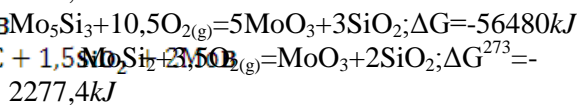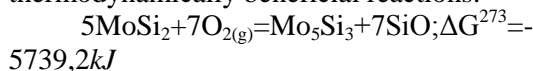
Conclusions:

It was found that the addition of molybdenum silicide increases the ZrB_2-based ceramics oxidation resistance by the formation of a $ZrSiO_4$needle-like structure and a SiO_2dense crystalline layer.

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FORMATION OF REFRACTORY METAL BORIDES DURING MECHANICAL ALLOYING

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Numerous studies have been devoted to production of transition metal borides using a mechanical alloying, but mechanisms of their formation are still under discussion. In particular, mechanical alloying of titanium diboride has been investigated widely enough, while the peculiarities of structure transformation under milling other transition metals with boron have not clarified yet. However, questions concerning the influence of the structure and atom size on the peculiarities of boride formation during mechanical alloying have been scarcely considered so far.

The transition metals of group IY Ti, Zr, and Hf have a hexagonal close -packed (*hcp*) structure while the transition metals V, Nb, and Ta refer to group V and have a body-centered (*bcc)* structure, which is characterized by a bigger free volume (space fill factors are 0.74 and 0.68, respectively). The group VI metals Cr, Mo, and W have a *bcc* structure as well but their atoms are much smaller compared to group V metals and possess a stronger interatomic bond, which is confirmed by far higher Young modulus. Therefore, a question arises: what phases can form at mechanosynthesis temperatures and how much is the phase formation dependent on the metal structure, the metal/boron atom size relationship and the peculiarities of mechanical allying process?

The aim of the work was to investigate the peculiarities of boride phases formation during milling powder mixtures of IV-VI group metals with boron at different Me:B atom ratios in a planetary mill AIR 015 M.

Powdered mixtures of transition IV -VI group metals with boron were milled in a planetary mill at a drum rotational speed of 1840 rev/min in an argon atmosphere. The balls-to-powder mass ratio was 20:1. XRD data and modeling for formation of boron-in-metal solid solutions showed that refractory borides of transition IV-V group metals are formed under mechanical alloying by two mechanisms:

1. Mechanically induced self-propagating reaction, determined by the enthalpy of refractory compound formation and the capability to form a substitutional solid solution.

2. 2Formation of interstitial boron-in-metal solid solutions, their subsequent decomposition and the appearance of the MeB2 phase.

Formation borides of VI group passes by mechanism formation of a new boride phase nuclei in the places of defects metal packing and their gradual growth.

REACTING INTERACTION IN COMPOSITIONS BASED ON REFRACTORY METALS AND SYSTEMS WITH DYNAMIC STABILITY CHARACTER

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Theoretical and experimental study of regularities of interaction processes in metal systems based on refractory metals with reacting components and compounds of various physico-chemical nature allowed to develop new ideas about the mechanisms of synthesis, reaction sintering, and to reveal a new class of systems with a dynamic character of stability [1, 2].

There are several types of nonequilibrium systems, which, by their kinetic features, are very different in their behavior. The most studied systems are those where the rate of interaction is determined by the processes of heterodiffusion. In such compositions, it is easy to control the degree of nonequilibrium and the compaction and structure formation processes.

Reaction systems with a kinetic nature of the interaction, the special case of which is, for example SHS, are characterized by the most complex nature of the behavior.

The application of new high-speed methods of experimental investigation of the thermo kinetics of reactionary interaction made it possible to establish the synergistic nature of the processes occurring and to reveal a new class of systems with a dynamic character of stability In this regard, all the reaction compositions can be attributed to two classes of physicochemical systems, namely: temporarily excitable and constantly excitable.

Temporarily excitable nonequilibrium systems have considerable free energy, the relaxation of which, when external energy is applied, should lead to an equilibrium state. However, due to external conditions or the choice of a particular kinetic law, for example, a nonlinear one, the system can freeze and maintain its nonequilibrium, which can only be destroyed by a much larger energy impact. In such systems, various types of behavior, such as detonation, superposition of thermal and concentration waves were discovered during the interaction, in the case of their initiation in various parts of the reaction mixture. All these processes determine the macro kinetics of sintering. The practical result of studying the synergetic nature of the interaction is the creation of a programmable technology of compaction and structure formation, in which the free energy of the system is spent to consolidate the composition.

Constantly excitable compositions with a dynamic character of stability were first found in systems based on metals of the IVA, VA groups of the periodic system, Cr and alloys containing these metals and their compounds with elements of the oxygen group [3]. These are dissipative systems, which by analogy with objects of living matter retain their nonequilibrium due to external energy flows.

The materials developed on the basis of such systems have a high level of functional properties when working under extreme conditions.

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Ti-C-V T-x-y DIAGRAM WITH THREE-PHASE REACTION TYPE CHANGING. COMPUTER-AIDED ALLOYS DESIGN

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Among the 3-phase regions in T-x-y diagrams there are encountered such, in which a change in the type of reaction occurs. The fact that change of the phase reaction type is not at constant temperature, but in a certain temperature interval, was for the first time proven in [1,2]. Later it was shown [3,4], that the special surface corresponds to the mass increment sign change in the each of three coexisting phases. This surface is ruled and is formed with the horizontal generating line (since the reaction of the 3-phase one is converted into the 2-phase one on this surface, i.e. it is possible to name it as the 2-phase reaction surface). The algorithm of the construction of the 2-phase reaction surfaces in the 3-phase regions is included to the software of the T-x-y diagrams 3D models design [5].

Change of the reaction type in the system Ti-C-V along the univariant curve, which corresponds to interaction of liquid and solid solutions Ti(V) and TiC($C_{0.9}$V), with the minimum of 1575°C was fixed experimentally [6]. However, in contrast to the assertion into [6], that "the tie-line, that corresponds to this minimum, is the boundary between the peritectic part of the diagram and the eutectic", in reality, the temperature of this transformation is not constant (1575°C) for the different alloys, but it changes over the surface of 2-phase reaction with L and Ti(V) with zero increment of the mass of TiC($C_{0.9}$V). Furthermore, with the aid of the Ti-C-V T-x-y diagram 3D model it was determined that the change in the phase reaction type from the peritectoid to the eutectoid has a place three times in the region Ti(V)+TiC($C_{0.9}$V)+CV$_2$ with three surfaces of 2-phase reactions.

3D models of the T-x-y digrams are very useful to verify the data interpretation, got by experiments and thermodynamic calculation [7-9].

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OVERCOMING OF BRITTLENESS OF MATERIALS BASED ON REFRACTORY COMPOUNDS

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Brittleness of the most materials based on refractory compounds (RC) limits their use as structural materials (SM). It is because of the brittleness that the data on the strength and other mechanical properties of the RC are largely speculative "the least reliable," as G.V. Samsonov noted [1]. Strength is not a characteristic of a particular RC. It is determined by the size of the defect in a specific SM sample and its fracture toughness (FT). Laboratory samples of SM can have high strength, which is practically impossible to achieve in real products and, moreover, to keep it in operation. Therefore, the most promising direction of creating SM based on the RC is to increase their FT.

The brittleness of materials is due primarily to the lack of plasticity. In this connection, in recent decades, the direction of study of regularities has been intensively developing, thanks to which SM, almost entirely consisting of a brittle component, have high FT, without regard to their chemical or phase composition [2]. For example, the material of a nacre shell possesses the fracture toughness, more than 3000 times the fracture toughness of calcite – the brittle component of which it is composed by 95%. The non-brittle behavior of biological SM during fracture is provided by a fibrous or layered structure with a sufficiently low shear strength along interfaces of layers/fibers. Unidirectional fibers and layers in the material are oriented in the direction of the maximum normal stresses acting on the structural element during operation. A new generation of artificial structural materials, namely, one-component materials with a unidirectional fibrous structure are being developed. They are practically 100 percent content of load-bearing elements – of fibers – in the structure, and therefore have the highest potential of strength properties. The most striking example is SiC-ceramics SA-Tyrannohex™ [3], which is almost 100% composed of fibers.

The figure shows a cross section of the model material obtained by hot pressing glass fiber bundle (top) and examples of its deformation diagrams (bottom) [2].

Importantly that the most people associate the glass with the brittleness. It should be noted that presented diagrams are the deformation diagrams of the glass without any additives as a matrix, a glue at the interfaces, etc. Therefore, investigation of transformation mechanisms of a brittle material into the quasi-plastic ones without changing the chemical and phase composition is very important to overcome the brittleness of materials as a whole and of RC in particular.

Thus, as a result of the analysis of known SM from low-plastic components, as well as numerical and experimental modeling of their fracture, it is shown that the most effective method of reducing brittleness is the formation in the material structure long interfaces with a sufficiently low inelastic shear resistance and parallel to the direction of the maximum normal stresses acting in the structural element during its operation.
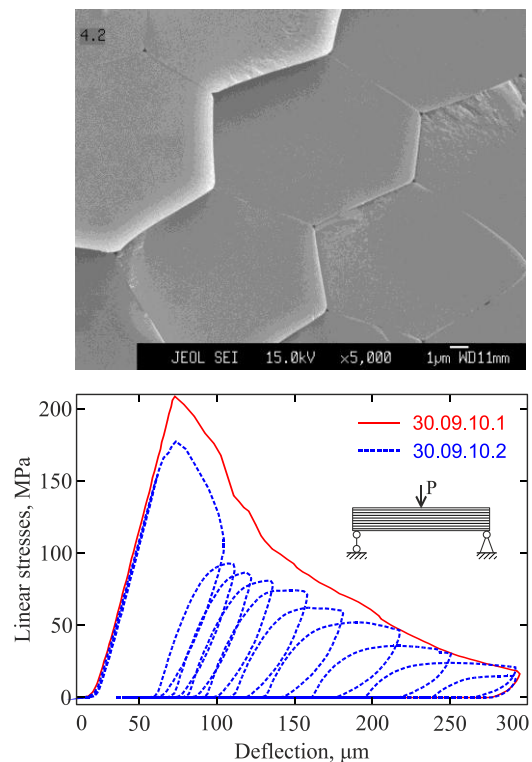
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INFLUENCE OF TCP ON THE DAMPING PROPERTIES OF THE CUTTING PLATESWITH HARD ALLOYS

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In the process of machining, the contact surface of the tool cutting edge, except for cutting forces, is subjected to vibrations arising in the technological system.This leads to appearance and development of fatigue cracks in the plate, which is the main reason of the failure cutting tool.

The damping ability of the material must be taken into account in the development of structural materials designed to work under shock fatigue loads.

The possibility of a resonance method to determine the damping ability directly on the cutting inserts makes it very promising as a comparative evaluation of the effectiveness application of various methods to improve their performance.

In connection with this, the main goal of the work was investigation the relationship between the structure parameters of solid alloys T5K10 and T15K6, damping properties and operational resistance at the cutting with replaceable cutting plates. Cutting plates in the initial state were subject to comparison and subjected to TCP under argon pressure 3,0 MPa.

Object of research: Hard alloys T5K10, T15K6, replaceable cutting plates SNUM 19716 produced by the "Pobedit" company, which are used respectively for the roughing and finishing of rolled billets of the wagon axles (HB 220-250), they are also thermocompressionprocessing(TCP) underargon pressure 3,0 MPa.

The subject of the research: establishing the relationship between the structure characteristics of T5K10, T15K6 alloys and the damping properties of cutting plates sintered by standard technology and subjected to TCP.

As an estimate of the damping ability of material the value of logarithmic decrement δ, which was determined by the resonance method, was used. To implement the method in the V. Bakul Institute for Superhard Materials of the National Academy of Sciences of Ukraine, an automated system was developed on the basis of the measuring stand "Sound-107"[1].

According to the experimental data, the residual microporosity in the structure of both alloys of different plates varies over a wide range. TCR not only reduces to the same extent, but also stabilizes microporosity and eliminates large pores. In addition, it slightly (up to 5%) increases the size of carbide grains in the structure of both alloys.The magnitude ofoscillations logarithmic decrement of the initial plates of T5K10 alloy is twice smaller that of the T15K6 plates. After TCP, the value of decrement for T5K10 alloy decreased by 30%, and T15K6 alloy decreased by 2 times. At that, the range of values decreased by 2,5 and 3,0 times, respectively.As can be seen, the decrease and stabilization of value δ ofplates from both alloys exposed to TCP, in this case, clearly correlates with a decrease in the residual microporosity and the elimination of large pores in their structure.Theresistancecoefficient $K_{CT}$of plates during cutting, as expected, directly depends on the degree of reduction of microporosity in hard alloys structure and back from their damping ability.

At the same time, there is no direct relationship between the degree of reduction δ and the resistance coefficient of the plates from T5K10 alloy during rough turning and from T15K6 alloy at the final cutting of the wagon axles, increased by 50% and 30% respectively.The correlation between the degree of decrease in structure porosity of alloys and the degree of decrease in oscillations logarithmic decrement is due to the fact that the residual pores, as a structure component of alloy, are able to dissipate the energy accumulated in the cutting process.

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STRUCTURAL STATE OF PRESSURELESS SINTERING MATERIALS AlN–Y$_2$O$_3$–(SiC–C)

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Because of its high thermophysical and dielectric properties aluminum nitride (AlN) is an object of investigation and applications as functional and high thermal conductive ceramics.

The aim of this study is the manufacture AlN-composite with addition of silicon carbide nanoparticles to intensify the formation of solid solution and corresponding decrease of silicon carbide particles size in the materials, the study of the structure of composites and the determination of the effect of structural characteristics on the hardness, thermal conductivity, and absorption of electromagnetic energy in the microwave range.

The pressureless sintering from powder compositions AlN–Y$_2$O$_3$ with the addition of 50 nm SiC-C nano-particles (200 nm agglomerates) the materials with a ceramic matrix of aluminum nitride were produced.

Raman (Fig. 1) and micro-X-ray analysis, as well as measurement of the microwave energy attenuation and thermal conductivity, has been established the formation of a solid solution of SiC in AlN.

Analysis of the composition of the grains of the composite was carried out with the help of MRSA (Fig. 2).

AlN, since carbon and silicon are present in all grains of the composite.

The main physico-mechanical properties of made AlN-(SiC-C)-composites are: Vickers hardness HV$_{147\,H}$ = 10.2-15.3 GPa; thermal conductivity of 35 W/(m·K) (see Table) and 44 W/(m·K), for materials with SiC-C content, respectively, 16 and 32 % (by weight); and the absorption of microwave energy in the 9.5-10.8 GHz band is 3.0, 7.5 and 11.5 dB/cm, respectively, with a starting SiC-C content of 16, 24 and 32 %.

Table – Half width of Raman peaks E$_2^{high}$ and thermal conductivities λ of AlN different genesis

Samples	HWP E$_2^{high}$ sm^{-1}	λ, W/m·K	Sour.
Hot-pressed with high temperature annealing polycr. AlN (reference)	9,5	53	p. 1
Pressureless sintered AlN–Y$_2$O$_3$–16(SiC–C)	76,2 75,0 79,1	35	p. 2, p. 3, p. 4
AlN single crystal	50,0	–	Perlin
Pressureless sintered polycrystalline AlN: without oxygen with 2,5 at.% oxygen	2,1 4,7	– –	McNeil
Pressureless sintered AlN without additives AlN with yttrium oxide	7,9 6,5	110 240	Lee

Fig. 1. Raman spectrum of the pressureless sintered AlN–Y$_2$O$_3$–16(SiC–C) composite
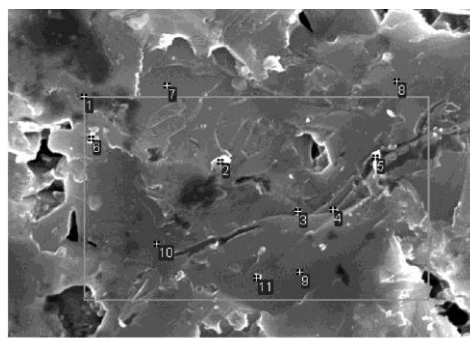
Fig. 2. Structure of the composite produced by pressureless sintering from AlN–Y$_2$O$_3$–(SiC–C) powder system; *1-11* - MRSA points

The MRSA data on the grains of the AlN-32(SiC-C) structure indicate that during the sintering of the AlN-Y$_2$O$_3$-(SiC-C) system, the SiC-C phase dissolves in the crystalline structure

ELECTRIC CONDUCTIVITY OF DIAMOND POLYCRYSTALS AND COMPOSITES DIAMOND - COPPER AND DIAMOND - COPPER – TITANIUM

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Composites diamond - copper and diamond - copper - titanium are composite materials in which the matrix is a sintered diamond powder, and a bond is copper or an alloy of copper and titanium. They were obtained by sintering in a high pressure apparatus at a pressure of 8 GPa and at a temperature of 1600 ° C. Diamond polycrystals were obtained by sintering a diamond powder without additives at the same temperature and pressure. In this article, the dependence of the electric resistance of diamond composite materials (DCM) on the time of sintering is investigated. Sintering time varied from 5 to 20 seconds. For all samples diamond granules 40/28 μm were used. The content of Cu in composite diamond-copper is 12% by volume (by weight ~ 26%). The ratio of components of DCM diamond - copper - titanium is shown in the table.

Table. The ratio of the component content of the composite diamond-copper-titanium.

	Volumetriccontent,%	Masscontent,%
Diamond	88	77,4
Ti	4	4,5
Cu	8	18

There is a sealing of the components of composite materials in the process of sintering under pressure, which leads to increased density and reduced porosity in them. Electrical conductivity is a sensitive characteristic of the material to the structural changes that occur in the process of obtaining such materials. The results of the measurement of the electric resistance of the DCM are shown in the figure.Diamond polycrystals, sintered without binder during 10 seconds, are isolator, and the electro resistivity of one is over 10^9Ohm·cm.The density of this materials are low (just around 73 % of theoretical value) [1], because of high porosity.Specific electro resistivity of polycrystals sharply reduced to value of tens Ohm·cm for polycristals sintered for the 15 – 20 seconds.At the same time, the density increases to 92% - 96%.Specific electro resistivity of cooper – diamond composite is almost un-changed with time of sintering in the interval 5 – 20 seconds, and has value within $0,7·10^{-2}– 1,4·10^{-2}$Ohm·cm, that

less than three orders of magnitude compared to Diamond polycrystals, sintered with-out binder during 15- 20 seconds.Analogic de-pendence of density on sintering time of this com-posite is described in [1]. She is almost not changed on time from value that obtained during 5 second of sintering, and is 93 % of the theoretical value.
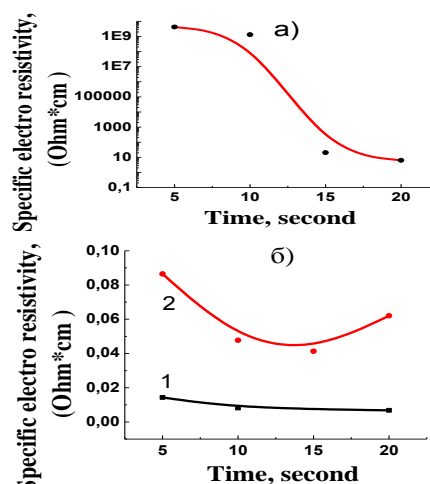
Figure - the dependence of the resistivity on the sintering time (a) of the diamond polycrystalline, (b) of composites: diamond-copper (1) and diamond-copper-titanium (2).

The specific electro resistivity of diamond-copper-titanium composites are higher that specific electro resistivity of diamond-copper composites and has value within $8,6·10^{-2}– 4,1·10^{-2}$Ohm·cm (Figure (b)). The electro resistivity of diamond-copper-titanium composite decreases at sintering process during 15 second, that are correspond to in-crease density of composite, that reaches a maxi-mum after 15 second sintering, and is 95 % of the theoretical value.Consequently, in such materials, the electrical resistance and sealing are interdependent.

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OF RESEARCH INFLUENCE OF GRAIN COMPOSITION OF THE MIXTURE ON THE DAMPING PROPERTIES OF POLYCRYSTALLINE SUPERHARD COMPOSITES OF THE SYSTEM WITH BN-AL

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Polycrystalline materials of cubic boron nitride (PCBN) in the world market are almost exclusively developed and manufactured for instrumental purposes in the form of cutting inserts, and one of the reasons hindering the widespread use of high-speed cutting processing methods are accompanying vibrations arising in the cutting zone of metals and often lead to accelerated and catastrophic wear of the tool [1].

Sintering of powders cBN with Al is a method of obtaining polycrystalline materials based on cubic boron nitride (PCBN), which is universally recognized in the world practice. A low melting point, and the formation of compounds based on Al (AlN, AlB2, AlB12) during sintering provides high crack resistance of polycrystalline grains.

The aim of this research is to study the influence of the grain size of the initial powders of cubic boron nitride on the physic-mechanical and damping properties of composites obtained by sintering powders of the cBN-Al system.

Sintering was carried out in a high-pressure steel apparatus called an anvil with a recess with a diameter of 40 mm. Output powders are cubic boron nitride of grade KM by grain size from 3/2 to 60/40 microns produced by the concern "ALKON" of the NAS of Ukraine, and aluminum powder of ASD grade, fraction - 40.

5 variants of the mixture were investigated: a) KM 3/2 + Al-40 (9: 1); b) KM 3/2 + KM 60/40 + Al-40 (7: 2: 1); c) KM 3/2 + KM 60/40 + Al-40 (9: 9: 2); d) KM 3/2 + KM 60/40 + Al-40 (2: 7: 1); e) KM 60/40 + Al-40 (9: 1).

The specific surface area of the cBN powder of grade KM 3/2 was 2.80 m^2/g, and the powder of KM 60/40 was 0.11 m^2/g. The specific surface area of the cBN powder for each mixture variant is shown in table. 1.

Table 1. Specific surface area of powders cBN

The mixture	*а*	*б*	*в*	*г*	*д*
S, м^2/г	2,80	2,2	1,46	0,71	0,11

As can be seen, with an increase in the fraction of coarse fraction, the specific surface area of powders cBN decreases.

Sintering occurred in two stages: 1) impregnation of Al at p = 2.5 GPa, T = 1100 K, 30 s, and 2) final sintering at p = 4.2 GPa, T = 1750 K, 240 s. The phase composition of the composites was determined by X-ray diffraction analysis using a "DRON-3" X-ray diffractometer. Damping properties (DP) were determined by an acoustic resonance method, and a logarithmic decrement of oscillations is presented as an estimate of these damping properties (the higher its value, the better is the DP of the samples).

Results:

Table 2. Density and hardness of samples

After sintering (4.2 GPa, 1750 K, 4 min.)					
The mixture	а	б	в	г	д
ρ, г/см^3	3,33	3,37	3,39	3,39	3,39
ρ, %	96,5	97,7	98,5	99,3	99,5
HKN, GPa	25	26	27	27	28
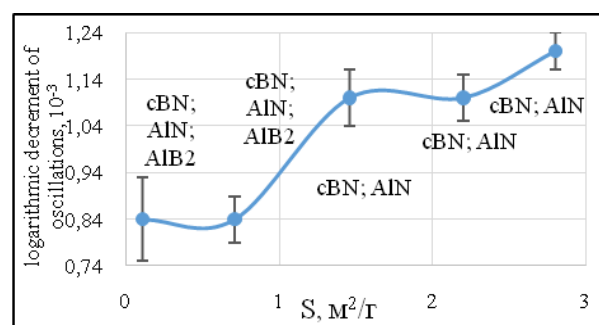
Figure - Dependence of the logarithmic decrement of vibration on the specific surface area of the composite cBN-Al.

The maximum values of the decrement of oscillations are achieved in composites obtained from powders of cBN with a grain size of 2 ± 3 μm. Possible causes - the maximum dispersion, the smallest density, the presence of solid solutions based on the AlN phase.

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RECEPTION OF NONSTANDARD HARD ALLOYS

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Hard alloys have a number of valuable physical and mechanical properties, the main of which is high hardness at high compressive strength.

Since cobalt powder is precious and uncommon, there is an urgent need for replacing cobalt with less scarce materials such as iron or nickel.

In the Fe-W-C system (Fig. 1), there is a four phase zone with three phases (graphite, Fe_3C, WC) solid and one liquid. The maximum solubility of WC in iron is 7-12 at 1250 ° C and in Fe-WC-W-Fe zone there can be two cubic and one hexagonal phases (Fe_6W_6C, Fe_3W_3C, FeW_3C carbides respectively) [1].
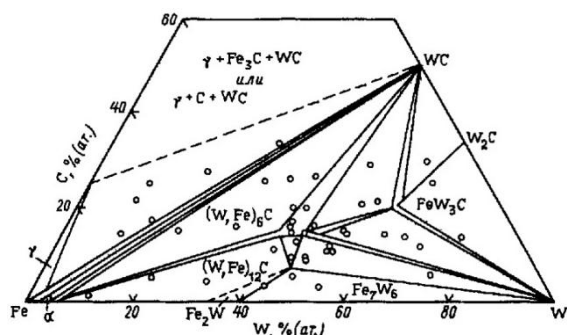
Figure 1 - Isotermic section of the Fe-W-C system at 1000 ° C

Although the strength in both cases is somewhat reduced, we obtain a material with sufficiently high properties at a lower cost of the original components. Additionally, powdered boron and copper carbide was injected.

The aim of the work is to obtain non-standard hard alloys in low vacuum and to study the main properties.

The mixtures of powders were rinsed in a planetary mill, sintering of specimens was carried out in an induction furnace at a temperature of 1450 ° C for 30 minutes with dilution (10 Pa).

A characteristic type of microstructure is depicted on (Figure 2). The material structure is heterogeneous and fine-grained with a carbide size of preferably 1-5 microns.

The analysis of properties indicates the passage of the active reaction during sintering, which is confirmed by the data on density and shrinkage, which range from 12.7 g/cm^3 to the alloy composition of WC - 6% wt. Fe - 2% wt.. B_4C and up to 13.6 g/cm^3 for WC - 6% wt. Fe - 2% wt. B_4C - 2% wt. Cu, shrinkage is in the range of 0.39 - 0.45%.
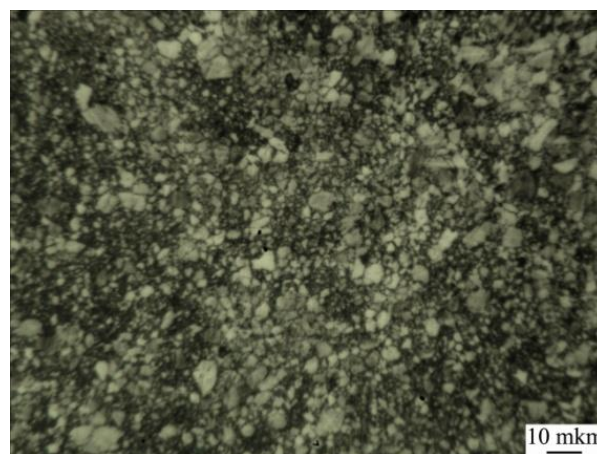
Figure 2 - Microstructure of sintered at 1450 ° C samples of WC - 6% wt. Fe - 2% wt. B_4C

The hardness is at the level of 85-86 HRA for the investigated compositions; the compressive strength has a larger interval due to its peculiarities. As is known, the main reason for reducing the strength of WC-Fe alloys is the ability of iron and nickel to dissolve tungsten carbide in solid state to form brittle carbides such as NiWC or $Fe_xW_xC_y$.

Samples of the WC system - 6% wt. Fe - 2% wt. B_4C have compressive strength - 1252 MPa. The highest compressive strength has alloys of the WC system - 6% wt. Fe - 2% wt. B_4C - 2% wt. Cu, which is 1704 MPa.

Thus, new warehouses of nonstandard hard alloys, vanished in low vacuum, were developed and investigated. It was found that samples of the composition of the WC - 6% wt. Fe - 2% wt. B_4C - 2% wt. have higher compressive strength at the same level of hardness.

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compressive strength

MULTILAYER COMPOSITES FROM SOLID ALLOYS ON TITANIUM CARBIDE BASE

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As a rule, for monolithic solid materials, there is a regularity: with increasing hardness, the fracture toughness decreases. To increase the fracture toughness (K_{Ic}) of hard and brittle materials, they are made in the form of composites, in particular layered [1]. In such systems, artificial internal stresses are created, which slow the spread of the crack and increase the K_{Ic} [2]. Solid alloys, in particular titanium carbide, also belong to materials with low fracture toughness [3].

In the proposed work, multilayer composites made of titanium carbide-based alloys were obtained. Their structure is studied and mechanical properties are studied. For compositions №. 1 and №. 2, a solid solution of the initial carbides (TiC, VC, Mo$_2$C, and NbC) was preliminarily obtained [4]. The composition of the initial mixtures of powders for individual layers of the composite is shown in the table.

After introduction of a 5% rubber solution in gasoline in a mixture of powders, pellets of less than 700 μm in size were obtained which were rolled into strips in a rolling mill of the "quarto" system with a horizontal arrangement of working and supporting rolls 40 and 110 mm in diameter, respectively. The resulting ribbons had a thickness of 0.45-0.55 mm and a relative density close to 0.5. Of these, plates were cut, which were laid in a suitable way and hot pressing was carried out at a pressure of 20 MPa at a temperature of 1450-1500 ° C, holding time of 8-10 minutes after complete shrinkage.

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Table

Chemical Composition of Mixtures

Mixture composition	TiC	VC	NbC	Mo$_2$C	Ni	Cr
№1	64,6	3,8	3,8	3,8	19,2	4,8
№2	69,7	4,1	4,1	4,1	14,4	3,6
№3	59,5	-	-	18,4	22,1*	-

*12,59 mas.% Ni и 9,51 mas.% NiO

а   *б*
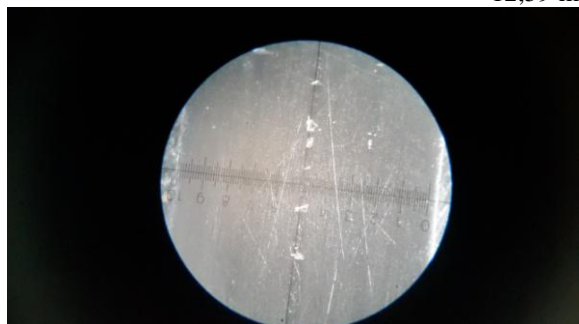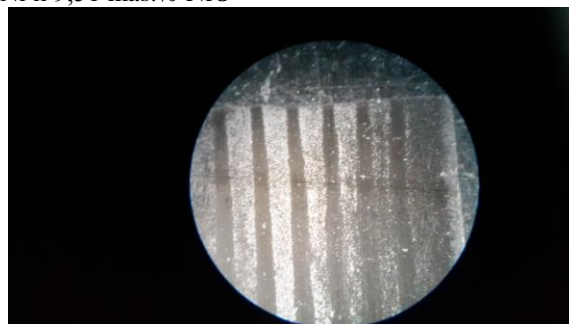
Figure - Metallographic images of composites in a plane perpendicular to the direction of the layers:
a) five-layer composite, b) a thirteen-layer composite

PRESSING OF CARBIDE MIXTURE

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Features of cold pressing of anoxic refractory compounds [1] and carbide mixtures [2] are of practical interest. Insufficient knowledge of the processes of cold pressing of carbide mixtures determined the purpose of this work - the study of pressing dry (ie, without plasticizer) blends VK6 and KHN25. These mixtures were pressed in a demountable mold with a diameter of 10 mm with a ratio H / d of the produced briquettes of at least 2.

It was preliminary established that the pressing of the mixtures in an ungreased mold takes place with vibration and pressure jumps, and the resulting briquettes show a tendency to a one to threefold stratification. Lubrication of the working surface of the mold with animal fat or engine oil reduced external contact friction, and, accordingly, eliminated the breakdown almost completely. onsidering the possible contribution of metals (Co, Ni) as a plastic constituent of carbide mixtures, a nonoxidizing annealing of the VC6 mixture at 950°C for 1 hour was carried out. It was found that the pressing of the annealed mixture in a lubricated mold invariably proceeds with a multiple briquette separation, which may be due to an increase in their elastic aftereffect. When compacting KHN25 at 700 MPa, well-reproducible porosity values of 38% were obtained, and when compressing VK6 mixture at pressures of 200, 400, 550 and 700 MPa the following values of porosity of briquettes were obtained: 48; 44; 42; 40%.

The pre-pressing of the obtained briquettes from the VK6 mixture was carried out in the same split mold, at a pressure of 700 MPa. It is established that the pre-pressing takes place without a breakdown with a slight decrease in porosity; so in briquettes compressed at 400 MPa and pre-pressed at 700 MPa, the porosity decreased from 44% to 40%.

The comparatively low technological strength of the briquettes produced, their propensity to fracture when pressing the mold due to a collision with the lower plate of the press, necessitated the development of a method for eliminating these drawbacks. For this purpose, the demountable mold used was installed on a steel tank with gasoline. In this case, when pressing out, the briquettes did not fall on a solid plate, but into gasoline, plunged to the bottom of the tank and soaked in gasoline. After impregnation, the briquettes were removed from the gasoline and placed on the bottom of the Alundum crucible in which they were subjected to natural or forced drying; after drying, the crucible with briquettes was placed in a vacuum oven and sintering was carried out. Thus, the described pressing procedure provided some increase in the strength of the briquette due to tightening capillary forces and included a single dynamic but gentle contact with the briquette, when it was extracted from gasoline and installed in a crucible.

The described experiments have shown that cold pressing of carbide mixtures containing riveted (and therefore not plastic) grinding metal microparticles, like pressing powders of refractory compounds, which do not show tendency to breakage due to low elastic aftereffect. Its increase, by annealing and, correspondingly, an increase in the plasticity of the metallic component, apparently initiates a breakdown. The ability to control the properties of briquettes from carbide mixtures obtained by pressing and then impregnating them with a well-wetting liquid may prove to be in demand in the manufacture of carbide-tipped products.

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SPARK PLASMA SINTERING OF MgAl$_2$O$_4$

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Polycrystalline ceramic materials (in particular, aluminum magnesium spinel) are able to retain their serviceability up to high (~ 1500 °C) temperatures under conditions of corrosive media and abrasive wear [1].

The maximum density of spinel can be reached either by using high-temperature sintering methods (accompanied by extreme grain growth) or by adjusting the sintering process with retaining the initial size of powder particles. Ceramics with high density can be used, e.g., for high-temperature high-transparency windows. In particular, spinel ceramics with a residual porosity of at most 0.01% must have a glassy appearance and high transmittance [2]. To obtain dense ceramics, it is necessary to use nanopowders and perform their sintering at sufficiently low temperatures to avoid significant grain growth. In this connection, the spark-plasma sintering method is promising

The possibility to control and regulate the heating rate of the material is an essential feature of the spark-plasma sintering method. The dynamic variation of the applied pressure in sintering makes it possible to further reduce the heat treatment temperature and control grain growth during sintering. Due to this, it is possible to obtain a high-density fine-grained material for a relatively short process time.

In the experiment, S25CRX aluminum magnesium spinel nanopowders (manufactured by Baikalox, France) and spinel powders synthesized by the method of co-deposition from salt solutions in the IPM of the NAS of Ukraine were used. Sintering by pulsed electric current was performed on a FAST / SPS unit (FCT-HP D 25/1, FCT Systeme GmbH, Germany).

Micrographs of microstructures of the initial aluminum magnesium spinel powder and material consolidated by spark-plasma sintering at
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a temperature of 1400 °C is shown in the figure. The particle size of the initial powder is 250 nm, the particle size after sintering is ~ 1–2 μm, i.e., under these sintering conditions the growth factor is 2–4.
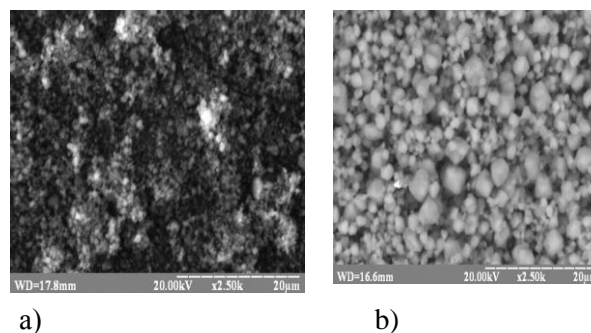
Figure 1 - microstructure of spinel:
a) initial powder, b) sample obtained by spark-plasma sintering.

As a result of the study, dense (99.5–99.8% of theoretical density) aluminum magnesium spinel ceramics from with a hardness of 13–14 GPa and a transparency of 80–85% in the wavelength range 3–6 μm was obtained.

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RESEARCH OF PHYSICAL AND CHEMICAL MECHANISM OF REACTION OF TiB$_2$ – TiN COMPOSITION SYNTHESIS

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The last years showed prospectivity of reactionary spark plasma sintering (RSPS) method of refractory compounds compositions, in particular TiB$_2$ - TiN [1], for the subsequent use them as cutting materials.

The thermogravimetric analysis (TA), differential thermal analysis (DTA) of the thermal treatment process of the TiH$_2$-B-hBN powder mixture and mass-spectroscopic analysis (MSA) of this thermal treatment products at the temperature of 20-1300°C were conducted with the purpose of determination of reaction way:

$$2TiH_2 + B + hBN \rightarrow TiB_2 + TiN + 2H_2 \uparrow \quad (1)$$
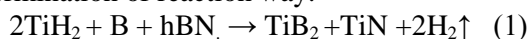
The components ratio corresponded to final content of TiB$_2$ 50 wt.% in TiB$_2$ - TiN composition.

The brown boron (company Merck, Germany) with the particles size of 330 нм was used. The powder mixture was sintered by the RSPS method at 1100 and 1700°C and the soaking of 0,5 min.

The release of physically bound water (~0,2 wt.%) occured at 80-150°C. The basic loss of mass (release of H$_2$) occured in the interval of 375-700°C. The amount of escaped H$_2$ made ~2,2 wt.%, i.e. ~ 0,2 wt.% hydrogen remained in the mixture, that corresponded to the chemical analysis results.

4 peaks were present on the DTA curve: 1 - 320, 2 - 450, 3 - 540, 4 - 660 ^{o}C. The 1th peak was related to the transition of the part of hydrogen atoms from tetrahedron to octahedral TiH$_2$ positions [2]. The process was endothermic, because energy of dehydrogenization activating of hydrogen atoms in tetrahedron positions (126,0 кJ/mol) considerably less than in octahedral (150,7 кJ/mol).

The 2th peak (450°C) was the result of hydrogen moving away from the tetrahedron pores. It could be related to more subzero value of the activating energy of hydrogen atoms in the tetrahedron pores as compared to the activating energy in the octahedral pores. Hydrogen moving away from the octahedral pores occurred at more high temperature (the 3th peak - 540°C), as this process was most laboured in terms of energy at TiH$_2$ thermal decomposition.

From the data [2], got as a result of nuclear magnetic resonance, even at 800°C, when TiH$_2$ practically fully has decomposed to metallic Ti, insignificant part of hydrogen still has been in the octahedral pores of the lattice. It was confirmed by the results of our researches. The 4th the least noticeable peak was related to the release of remaining hydrogen from the octahedral pores and by the reduction by the atomic hydrogen of B$_2$O$_3$ oxide.

The curve of MSA signals of H$_2$O practically fully repeated the DTA curve except for the 1th peak, the curve of H$_2$ - except for the water loss peak and the 1th peak. The intensity of ionic current signals of the H$_2$O exit made ~0,3% of corresponding H$_2$ intensity. The relative intensity of the CO$_2$ and CH$_4$ exit was less yet (~0,005-0,02%), however on all these curves the peaks have been visible virtually corresponding to the peaks 2-4 of H$_2$ release.

The basic crystalline phase was initial hBN, and TiN, TiN$_{0.3}$, TiB$_2$, TiB phases appeared after the sintering at 1100°C according to X-ray phase analysis data. TiB$_2$-TiN composition appeared with hBN tracks after the sintering at 1700°C.

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COMPOSITE MATERIAL BASED ON THE SYSTEM COPPER – WOLFRAM FOR CUMULATIVE CHARGES

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One of the promising directions for increasing the breakthrough action of a cumulative charge for economic or military purposes is the creation of a cumulative effect at the expense of the cone material of a cumulative charge [1].

Using a cone from a powder material of a cumulative charge will reduce the energy consumption of the charge by breaking the contact between the particles of the material and their reorientation into the flow.

This will increase the breakthrough capacity and the depth of breakdown [2, 3].

Increasing the flow energy of the cumulative jet can be by adding a powder mixture based on copper to wolfram particles with a melting point above 3400 °C.

The purpose of the work is to study the structure and physical and mechanical properties of powder material of copper - tungsten made by cold double-sided pressing.

The structure was studied using a raster microscope "Supperprob-723".

Metallographic studies have revealed the uneven distribution of t wolfram particles in the volume of the conical product.

The reason for this is the difference in the density of tungsten (19.3 g/cm^3) and copper (8.96 g/cm^3), the ratio of the size and morphology of the particles.

It was also established that the structure of the presses with the ratio of the particle size of the components of R (Cu) / R (W) = 4 is characterized by the presence of bundle cracks.

The reason for this is the factor of elastic aftereffect after pressing.

In the ratio of the particle size R (Cu)/R (W) = 0,4, the structure of the non-sintered product of the same composition is characterized by the absence of cracks, the presence of a greater contact zone of mechanical origin between the particles.

In the work also studies were carried out on the dependence of physical and mechanical properties of non-sintered material on the basis of the system of copper- wolfram on the content of (20-50 wt.% W) and dispersion (10-100 microns) of wolfram, as well as the height of the conical product (1/30 - 1/7 L).

It has been established that increasing the dispersion of tungsten leads to a decrease in porosity, but at the same time the values of strength (from 52 to 5 MPa) and the elastic modulus (from 35 to 11 GPa) are reduced.

In a non-sintered state, with a maximum pressing pressure, the average value of the product density of Cu is 50 wt. % W is 8.24 g/cm^3 ($\theta \sim$ 30%).

The bending strength (σ) is 27.3 MPa and the elastic modulus (E) is 30.0 GPa.

Increasing the pressing force to achieve greater density of samples leads to their destruction.

The density is 9,01 g/cm^3 ($\theta \sim$ 9%) mixture of Cu - 20 wt. % W at the maximum pressing pressure.

The average bending strength and modulus of elasticity are 21.2 MPa and 26.4 GPa, respectively.

Durability of bending samples of Cu - 20 wt. % W does not significantly depend on the height of the product.

The modulus of elasticity differs approximately in 2 times with an increase in height from 1/30 L to 1/7 L and is 14.7 and 9.6 MPa, respectively.

Increasing the porosity of the product leads to a predicted decrease in their strength and plasticity.

Thus, the maximum strength is the powder products of Cu - 20 wt. % W with porosity of 20 %. Samples with a porosity of 10 % have a partial bundle, which is the result of their trans pressing.

Physical and mechanical properties of powder non-sintered product of Cu - 20 wt. % W have lower rates than products made from a powder mixture of Cu - 50 wt. % W.

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WITHOUT OXIDIZING SUTTING OF THE COMPOSITION CAST IRON - ALLOY WC-6, PROPERTIES AND STRUCTURE

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There are many technological schemes for obtaining wear-resistant materials based on a plastic matrix with inclusions of tungsten carbide.

The purpose of the presented work is the development of technology for obtaining a heterogeneous wear-resistant material based on the waste of VK and synthetic cast iron alloys.

The heterogeneous material was obtained by sintering in the non-oxidizing medium [1] of the cast iron-VK-6 alloy composition at 1200 ° C for 1 hour. Composition of synthetic iron (wt.%): 4 - graphite, 5 - ferromanganese, st. - iron. The material structure is shown in Fig. 1 and consists of three regions: a directly solid alloy in the center, a transition zone and synthetic cast iron, due to the dissolution of the constituent elements of the hard alloy in the resulting cast iron.

Fig. 1. Sintered macrocomposite cast iron - hard alloy

The VK-6 hard alloy is a WC particle in a cobalt matrix and retains its properties to a temperature of 1150 °C. Since sintering was carried out at 1200 °C, diffusion of the elements of the hard alloy was observed. On the surface of the hard alloy, a layer 10-15 μm in thickness is formed on the basis of cobalt depleted in tungsten and enriched in iron and partly by manganese because of their diffusion from the cast iron. This occurs as a result of the difference in the rate of diffusion of tungsten and cobalt into the cast iron. As a result of sintering the cast iron-hard alloy composite, a uniform distribution of manganese in the material is also observed because of its high diffusion rate.

The thickness of the transition zone is up to 0.5 mm. It is an iron base with evenly distributed light carbide inclusions based on tungsten (Fig. 2).
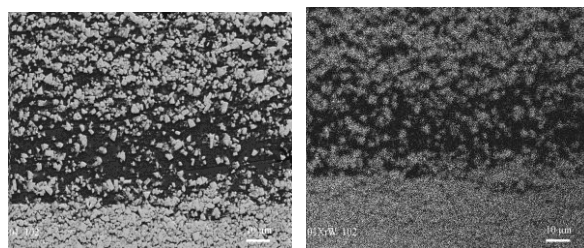
Fig.2. Structure of the interface of a hard alloy - cast iron

The average grain size of the high-melting carbide component in cast iron was from micron to 5 microns. Thus, as a result of sintering, iron is alloyed with tungsten and partly with cobalt.

The hardness of VK alloys is 87-92 HRC. The hardness of the VK-6 alloy after sintering was 71 HPC, and the cast iron - 51 HPC. The micro hardness of the cast iron-hard alloy composite (load 50 g) decreases from 12.4-15.4 GPa to 4.2 GPa on the surface of the hard alloy, which is due to a decrease in the tungsten content, and further increases to 5.6 GPa, which is the consequence increase in the content of tungsten carbide in cast iron due to diffusion.

The experiments carried out showed that the lump waste of hard alloys of the VC group can be used for the production of wear-resistant macro-composite products. This is quite obvious, since these alloys are well wetted with cast iron and, most importantly, have a higher density, which keeps them in submerged state when the mold is filled with molten iron.

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INVESTIGATION OF THE INTERACTION OF SILICON NITRIDE WITH ZIRCONIUM IN VACUUM

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Siliconnitride, along with aunique complex of physico-mechanical properties, exhibits high heat resistance and chemical stability under conditions of high temperatures and corrosive media[1]. However, thehigh-temperature stability of Si_3N_4 in protectiv media (nitrogenandargon) in contact with metals, particularly transition metals, decreases by a factor of almost 2 as a result of solid-phase interaction and the formationof refractory compounds of the metal on the contact boundary [2].The aim of the present work is to investigate the solid-phas in teraction of powder mixtures of Si_3N_4 with zirconium in vacuum in the temperature range (750–1450) °C. The regularity of the interaction was controlled by the methods of X-ray and chemical analyses.

The phase compositionofpowders obtained in vacuum with holding for 1 h at the indicated temperatures and the nitrogen content in them are presented in the table.

Temperature, °C	Phase composition	Nitrogen content, mass %
755	α–Si_3N_4, α–$ZrN_{0.28}$	9.7
1000	α–Zr_2N, α–Si_3N_4, ZrN, Zr_2Si, ZrSi	9.8
1450	ZrN, $ZrSi_2$, ZrSi	8.2

The investigation of the behavior of here action mixture in vacuum under the action of the temperature factor showed that, already atatemperature of 750 °C, the solid-phase interaction on grain boundaries of zirconium and silicon nitride occurred. According to the X-ray analysisdata, atatemperature of7 50°C, the formation of the solid solution of nitrogeninzirconium (α–$ZrN_{0.28}$) occurs due to contact diffusion. According to the literature data, the solubility of nitrogeninα–Zrin this temperature range is equal to 4.8 mass %. An increase in the interaction temperature up to 1000 °C leads to the formation of zirconiumnitride and zirconium silicide phases as are sultof the contact diffusion of silicon into zirconium. At a temperature of 1450 °C, the complete decomposition of silicon nitride occurs, and the main phases are ZrN and $ZrSi_2$. The chemical analysis data indicatethat then itro gencontentin the products of the solid-phase interactionat temperatures of 750 and 1000 °C is retained and is equal to the nitrogen content in the initial reaction mixture 9.8 mass%. At the same time, the presence of nitride phases of zirconiumin the interaction product sindicatesthatthede composition of silicon nitride and the contact diffusion of nitrogen and silicon into zirconium (at a temperature of 1000 °C) take place. In the composition of the products of interaction at a temperatureof 1450 °C, the well-formed ZrN phaseand zirconium silicide phases are present.According to the chemical analysis data, the nitrogen content is equal to 8.2 mass %. Thein significant decrease in the content of nitrogen as compared to its contentinthe initial reaction mixture shows that practically the whole amount of nitrogen takes part in the solid-phase interaction, and its lossesdue to high vacuum are small and equal to 1.6 mass %.

Ananalysis of the obtained data on the study of processesproceeding during high-temperature interaction in vacuum has shown that, at a temperature of 750 °C, the beginning of the decomposition of Si_3N_4 on the contact boundary with the metal takes place,which is evidenced by the formation of α–$ZrN_{0.28}$. Thein creasein the temperature up to 1450 °Cleads to its complete decomposition and formation of the refractory zirconium compoundsZrN and $ZrSi_2$.

In viewof the obtained results, it is reasonable to investigate the possibility of obtaining a composite material ZrN–Si_3N_4 by way of feeding nitrogen after holding for 1 h at 1000 °C in vacuum, which, in our opinion, will block the formation of silicide phases of zirconium.

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PREPARATION OF COMPOSITE POWDERS BASED ON TITANIUM BORIDE AND SILICIDES OF TRANSITION METALS

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The process of obtain ingcompositions based on titanium diboride with silicides of Groups IV-VI transition metalsof the periodic system in the mechanochemical reactor from elements was investigated. This choice of the initialsubstances makesit possible to obtain composite powders with a more uniform distribution of phases than in the case of synthesis from titanium boride and silicide.

There sult sof the present investigation show that titanium diboride, which forms by the explosive mechanism, initiates and intensifies the formation of silicide phases in all systems. DisilicidesofV, Nb, and Crformed for 5–15 min, where a sinthethersystems, the process proceeded for 30 min through the stage of formation of lower silicides (Me_5Si_3), the traces of which remained in products of mechanochemical synthesis (MCS). The formation of these intermediate phases is possibly caused by the high adiabatic temperature[1]. Since the systemsurmounts the corresponding energy barrier, phases form for a short time. According to the literature data and resultsofour investigations, theformationofTiB$_2$in the process of MCS proceeds by the reaction of mechanochemical "explosion"(stepwise increase in the degree of transformation of initial substances to the final product). The thermodynamic conditions favoring the mechanochemical "explosion" include the disturbance of the thermal balance of the system andthe fulfillment of the inequality $T_{ad} > T_{melt}$for the metal (e.g., for titanium diboride,T_{ad}= 3190 K, and for titanium,T_{melt} = 1941 K[2]). The formation o fTiB$_2$ by the explosive mechanism during MCS occurs with the large "ejection" of energy into the environment, providinghigh heat release, which obviously initiates the formation of silicide phases for 5–10 min.

To check this assumption, the MCS of the initial mixtures with different titanium diboride contentsin the composite powder was performed by the exampleof theTiB$_2$–CrSi$_2$ system. Itisseenfromthe presented data that it is impossible to obtain TiB$_2$–CrSi$_2$two-phase composite powder in the case where the content of the silicide phase is increasedabove 20 mass %. In all cases, the reaction products consist of a mixture of titanium diboride, chromium disilicide, the lower disilicide phase Cr$_5$Si$_3$and impurity of free silicon. Inthiscase, inthepowdersobtained by the MCS method, the amount of TiB$_2$ decreases. Nevertheless, the amount of the energy released during the explosive MCS ofTiB$_2$is evidently sufficient for the beginning of formation of silicide phases.

Calculated composition, mass %	Time of MCS, min	Phase composition
TiB$_2$–30CrSi$_2$	5	TiB$_2$, Cr$_5$Si$_3$, CrSi$_2$
	10	-"-
	15	-"-
	30	-"-
TiB$_2$–40CrSi$_2$	5	TiB$_2$, Cr$_5$Si$_3$, Si
	10	-"-
	15	TiB$_2$, Cr$_5$Si$_3$, CrSi$_2$
	30	-"-
TiB$_2$–50CrSi$_2$	5	Cr$_5$Si$_3$, CrSi$_2$,TiB$_2$, Si
	10	-"-
	15	TiB$_2$, Cr$_5$Si$_3$, CrSi$_2$, Si
	30	-"-

Thespecificsurfaceoftheobtainedpowdersrange sfrom 2 upto 5 m^2/g. With increase in the time ofMCS, its value rises due to the refinement of the formed phases during their subsequent treatment.

According to transmission electron microscopy data, thepowder of composition TiB$_2$–20 mass %CrSi$_2$ consists of titanium diboride and chromium disilicide.

Powderparticles have an irregular shape with a partial faceting. Theparticlesizerangesfrom 40 to 70 nm. The largest part of particles has a polycrystalline structure, but individual particles are single crystals.

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OBTAINING OF NANODIMENSIONAL POWDERS OF SOLID SOLUTIONS $Cr_{0,9}Ti_{0,1}Si_2$ AND $Cr_{0,9}Ta_{0,1}Si_2$

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Our previous studies of the mechanisms of $TiSi_2$, $TaSi_2$ and $CrSi_2$ mehanosynthesis showed that their formation at high-energy machining takes place by the mechanism of solid-phase diffusion (SD) without the formation of intermediate lower silicide phases. This suggests that the formation of solid solutions based on $CrSi_2$ in the process of mechanosynthesis will also occur according to the mechanism of SD.

High-energy machining of the reaction mixtures of the initial components, expected for the production of $Cr_{0,9}Ti_{0,1}Si_2$ and $Cr_{0,9}Ta_{0,1}Si_2$, was carried out in a planetary mill "Pulverizette-6" during 20 h.

According to X-ray analysis of machining products, solid-phase interaction takes place, as evidenced by well-formed diffraction peaks of the $TiSi_2$, $TaSi_2$ and $CrSi_2$ phases. In addition, the presence of the starting metals (Ta, Ti, Cr) is observed. The lack of diffraction peaks of silicon, in our view, related to its long-amorphization by 20 hours of machining. The phase composition of the products of machining is a mixture of initial components and individual disilicides. A homogeneous product requires long machining, leading to contamination of iron (up to 6-7% wt.). This suggests the use of inappropriate mehanosynthesis to produce nanosized powders of solid solutions.

Thus, it is possible to solve the problem if low-temperature synthesis is used in a vacuum of pre-mechanically activated mixtures. In this case, the purpose of machining is to increase the reactivity of the charge by crushing the powder and accumulation of defects in its structure, but the degree of activation does not allow the passage of chemical reactions.

Investigation of the influence of the temperature factor on the process of solid phase interaction of reactive charges in a vacuum was carried out in the temperature range 400-1000 ° C.

The figure shows the change in the intensity of the diffraction peaks of elements (Ta, Cr, Si) of the initial mechanically activated mixture $Cr_{0,9}Ta_{0,1}Si_2$ and products of solid phase interaction under temperature influence.

X-ray diffraction analysis shows that the formation of $Cr_{0,9}Ta_{0,1}Si_2$ solid solution is already observed at 800 ° C - as evidenced by the change in the phase of the phase lattice on the basis of $CrSi_2$, namely, their monotonic increase compared to the table values.
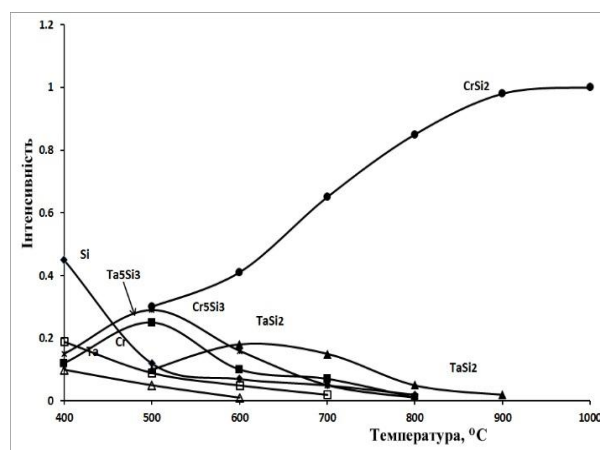
In turn, at 1000 ° C, the products of the interaction consist of a phase based on $CrSi_2$ with traces of silicon (one weak diffraction maximum), where the lattice periods correspond to a solid $Cr_{0,9}Ta_{0,1}Si_2$ solution.

Patterns of formation of $Cr_{0,9}Ti_{0,1}Si_2$ solid solutions are similar.

Our study showed that previous mechanical activation significantly affect the kinetics of passing SD, reducing the temperature as the beginning and end interaction at 300-400 ° C. This ensures the production of powder $Cr_{0,9}Ti_{0,1}Si_2$ and $Cr_{0,9}Ta_{0,1}Si_2$ solid solutions with an average particle size of up to 100 nm.

FEATURES OF SYNTHESIS OF NANO-DIMENSIONAL POWDERS OF SOLID SOLUTIONS ON THE BASIS OF MOSi$_2$ WITH TRANSITIONAL METALS

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Our previous studies of the formation of disilicides of transition metals in the process of mechanosynthesis have shown that depending on the level of the exothermic reaction of their formation, the interaction takes place in two mechanisms: solid phase diffusion (SD) and mechanically stimulated reaction (MSR). The authors of work [1] consider the criterion for determining the mechanism of reaction in the process of mechanosynthesis, as in the case of the usual self-extending synthesis reaction, the value of the adiabatic temperature, which must exceed 1800 K. On the basis of experimental data, the authors [2] have shown that the ratio of the heat of reaction and the specific heat of the product at room temperature $\Delta H_{298}/C_{298}$ correlates well with the values of the adiabatic temperature. We have found that the formation of molybdenum disilicide during mechanosynthesis proceeds by the mechanism of MSR. It allows to expect that solid solutions based on MoSi$_2$: Mo$_{0,9}$Nb$_{0,1}$Si$_2$ (T$_{adiab.}$ = 1891 K), Mo$_{0,9}$Cr$_{0,1}$Si$_2$ (T$_{adiab}$ = 1854 K), and Mo$_{0,9}$W$_{0,1}$Si$_2$ (T$_{adiab.}$ = 1842 K) in the process of mechanosynthesis by the mechanism of MSR will also be formed .

The aim of the work is to determine the specifics of the formation of solid solutions based on MoSi2 in the process of mechanosynthesis in planetary mills of different types.
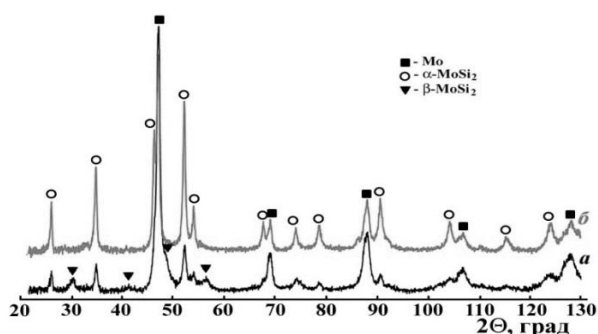
In fig. it is shown X-Ray pattern of the products of the mechanistic synthesis Mo$_{0,9}$W$_{0,1}$Si$_2$ in planetary mills "Pulverizette-6" for 20 hours (a) and "AIR-0,015" within 90 minutes (b).
The similar picture of X-rays is peculiar also for Mo$_{0,9}$W$_{0,1}$Si$_2$, Mo$_{0,9}$Cr$_{0,1}$Si$_2$.

The character of the X-ray of the products of mechanosynthesis, regardless of the conditions of machining, indicates the unbalanced and stressed states of the system, in which there are well-formed phases α-MoSi$_2$, β-MoSi$_2$ ("Pulverizette-6") and α-MoSi$_2$ ("AIR-0.015"), with a small amount of molybdenum. At the same time, the absence of the phase of WSi$_2$ (NbSi$_2$ and CrSi$_2$ in the case of solid solutions Mo$_{0,9}$Nb$_{0,1}$Si$_2$ and Mo$_{0,9}$Cr$_{0,1}$Si$_2$), as well as the change in the periods of the molybdenum disilicide lattice, indicate the formation of MoSi$_2$-based solid solutions.

It was established that in the conditions of the planetary mill "Pulverizette-6" (rotational speed 400 rpm) solid solutions are formed on the new molybdenum disilicide Mo$_{0,9}$Cr$_{0,1}$Si$_2$, Mo$_{0,9}$Nb$_{0,1}$Si$_2$ and Mo$_{0,9}$W$_{0,1}$Si$_2$. It was shown that the degree of completeness of the mechanochemical reaction process decreases depending on the presence of metals with higher melting points in the reaction mixtures than in Cr, namely, Nb and W.

While in the conditions of the high-energy planetary mill "AIR-0.015" (speed of 1370 rpm) a more complete passage of the MSR reaction is provided, with the time of machining to achieve the necessary results reduced by almost 10 times. This creates conditions for a more complete mechanical and chemical reaction.

Thus, it was shown that the mechanistic synthesis of solid solutions based on MoSi$_2$ with T$_{adiab}$ more than 1800 K due to the high exothermicity of the reaction by formation the compounds takes place in the MSR mode and allows to obtain nanopowders, whose coherent scattering region is 15-30 nm.

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INFLUENCE OF CRYSTALIZATION SPEED ON THE STRUCTURE OF THE METAL-CERAMIC COMPOSITE ON THE BASIS OF TITAN

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Titanium alloys with high specific strength and corrosion resistance are indispensable structural materials for the power, aerospace and chemical industries. In order to increase the strength and heat resistance of titanium and alloys on its basis, the most commonly used doping. An alternative approach to improving the mechanical characteristics of titanium is its reinforcement. A promising candidate as a reinforcing additive may be titanium boride, since it has a high Young modulus, strength, hardness and thermal expansion close to titanium.Composite materials of the Ti-B system are intensively studied in recent decades, while most of the work is devoted to composites obtained using powder metallurgy. The application of traditional metallurgical methods for the production of such alloys makes it possible to significantly reduce the cost of material and expand its applications.For the experiment, the titanium sponge TG-90 and TiB2 powder in the ratio of 94.7% by weight and 5.3% by weight were used. Long-length billets with a diameter of 10 mm and a length of 145 mm were formed on a hydraulic press in a collapsible mold at a pressure of 100 MPa. Directional crystallization was carried out in the induction high-frequency installation "Crystal 206" in a medium of excessive helium105 Pa. The rate of crystallization was:1mm/min, 2mm/min, 3mm/min, and 4mm/min.The method of X-ray diffraction analysis showed that the alloy obtained throughout the range of crystallization rates consists of two phases: titanium and titanium monoboride. Thus, it has been proved that during the crystallisation a chemical interaction between titanium and titanium diboride occurs with the formation of titanium monoboride, as evidenced by the Ti-B system fluctuation diagram.The study of microstructure showed that the crystallized alloy directed is a titanium matrix directed to a titanium monoboride reinforced.The influence of crystallization rate on the formation of microstructure of reinforced Ti-TiB metal-ceramic composite has been investigated. It was established that increasing the rate of crystallization leads to a change in the microstructure, namely, the higher the rate of crystallization, the smaller the size of the fibers, and their number is greater. With an increase in the crystallization rate from 1mm/min., up to 4mm/min the amount of fibers in the alloy increases from 16% to 37%.

INFLUENCE OF MAGNETIC-ABRASIVE TREATMENT ON MORPHOLOGY AND PROPERTIES OF SURFACE LAYER OF THE SOLID ALLOYED TOOLS

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One of the most promising methods for improving the working capacity of a hard alloy tool is magnetic abrasive teratment (MAT). The use of MAT ensures high purity of working surfaces, formation of optimal microgeometry of cutting edges, increase of their physicomechanical characteristics [1, 2]. At the same time, as a result of microplastic deformation under the influence of a magnetic abrasive tool (MAt), the structure, chemical composition and surface properties change.

This research shows that the magnetic abrasive treatment does not change the phase composition of the surface layers of hard alloys, but changes the quantitative ratio of the phases. So the content of Co on the surface after MAT increases, in comparison with that indicated in the brand, by 0.5-4.0% by weight, depending on the composition of the alloy, then falls by 0.5-2% by weight below the average at a depth of 100-150 microns and rises to normal as the distance from the surface is 250-400 microns.

Under the influence of impacts of particles of a magnetic abrasive tool at depths of up to 15 microns, intensive grain refinement was observed. The WC phase is especially strongly crushed - up to 1-2 microns in comparison with 3.5-5 microns in the core. This is due to its high fragility.

It was noted in [3] that, as a result of the thermomagnetic abrasive treatment, the structure of the surface layer had a coarse-grained structure and contained the elements compraised the MAt (for example, Fe). In our case, in no MAP modes, the surface layer did not form a coarse-grained structure. The low temperature (the temperature of the sample on the surface does not exceed 100 °C), during MAT in all treatment modes used, the possibility of adhesion interaction between the processed alloy and the constituent elements of the MAt was minimized.

MAT is accompanied by complex phenomena, which include, first of all, microcutting, micro-impact, plastic deformation. A particularly important role in the process of changing the properties of the processing surfaces is played by micro-impacts and plastic deformation, which determine the depth and microhardness of the hardened zone. The depth of hardening depends both on the hardness of the carbide compound, which is the main in the alloy, and on the amount of complex carbide (Ti, W) C or (Ti, Ta, W) C in the alloy structure (Table 1).

Table 1

Effect of hard alloy composition on hardening

Alloy	Content of complex carbide,%	Depth of hardening, microns	Microhardness, GPa
VK8	-	250	25,5
T15K6	~50	550	26,0
TT10K8	~38-40	400	27,0

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FORMATION of MULTICOMPONENT STRUCTURE of ZrB_2-BASED UHTC in ZrB_2-$ZrSiO_4$-C SYSTEM under REACTIVE HOT PRESSING

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The tasks of modern materials science are the creation of refractory composite materials with a high level of structural and operational properties.

In the work, studies of the reaction sintering processes and phase formation of ZrB_2-$ZrSiO_4$-C system ultra-hightemperature ceramics (UHTC) have been carried out.

X-Ray phase analysis was performed on a Dron-1 diffractometer in CuK_α radiation. Microstructural analysis has been made on a scanning electron microscope "Jeole".

With the help of thermodynamic analysis of zirconium concentrate ($ZrSiO_4$) carbon-thermal reduction reactions, the conditions that provide the preferential formation of SiC and ZrC carbides by the reaction:

$$ZrSiO_4 + 6C \rightarrow ZrC + SiC + 4CO_{(g)}$$

have been determined.

During the reaction sintering, a gradual shrinkage corresponding to the decomposition of $ZrSiO_4$ was observed, beginning from 1200 °C and increasing with the temperature rise. Significant shrinkage was observed at 1670-1800 °C, which corresponds to the intensive phase formation. A considerable shrinkage and porosity were observed up to the complete reaction passage during the sintering under pressure at a temperature of 2100 °C.

The data of X-Ray phase and microstructural analyzes revealed the presence of the main phase of ZrB_2 along with the formed SiC and ZrC phases.

Figure 1 shows a fracture of ZrB_2-ZrC-SiC ceramic obtained under reaction hot pressing. The morphology of the fracture represents particles of polycrystals of similar size and uniformly distributed throughout the volume.

Optimal conditions of ZrB_2-ZrC-SiC ceramic formation under reaction hot pressing have been determined.

The combination of carbothermal synthesis using $ZrSiO_4$ and ceramics hot pressing allowed to form a composite with a uniform distribution of ZrB_2 + ZrC + SiC components at a single process.
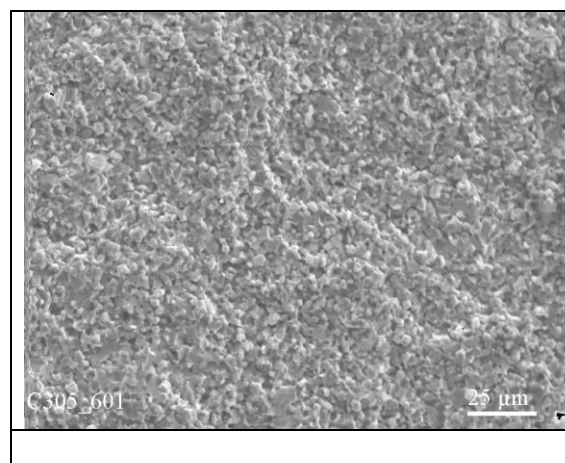
Fig.1 The image of fracture of ZrB_2-ZrC-SiC system UHTC.

LIQUIDUS SURFACE FOR THE Al_2O_3–TiO_2–Y_2O_3 PHASE DIAGRAM

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One of the main directions of the development of modern materials science is the development of new oxide ceramic materials for engineering, energy, chemical, aerospace, electronic and other industries in multi component systems, including with the participation of TiO_2, Al_2O_3 and rare earth oxides.

The Al_2O_3–TiO_2–Y_2O_3 system attracts the attention of researchers in connection with the possibility of obtaining on its basis structural high-temperature materials with low coefficient of thermal expansion, as well as refractory ceramic materials. The basis of the creation of new materials is the study of physical and chemical interaction, which is reflected in the diagrams of the state of the systems.

Authors [1] have studied isothermal sections of the phase diagram at 1400 and 1550 °C. No ternary compounds and appreciable solid solution regions on the base of components or binary compounds were found in the ternary system.

The aim of the investigation is to study phase equilibria during alloy crystallization in the Al_2O_3–TiO_2–Y_2O_3 system and on the base of the results derived construct the liquidus projection of the phase diagram on the concentration triangle.

Sample compositions were taken into consideration the results of interaction investigation in the system Al_2O_3–TiO_2–Y_2O_3 [1] and literature data about binary bounding systems.

Samples for the investigation were prepared by mixing starting oxides (ceramic method).

In a figure the results obtained are shown as a projection of liquidus surface of the Al_2O_3–TiO_2–Y_2O_3 phase diagram on the concentration triangle.

The liquidus surface of the Al_2O_3–TiO_2–Y_2O_3 phase diagram is constructed of the first time. The liquidus surface is consists there are eleven fields of primary crystallization of the phases of TiO_2, H-, C- crystalline

modifications Y_2O_3 and α-AT, β-AT, AL, YT_2, F, Y_3A_5, YA and Y_2A phases. Six four-phase invariant eutectic equilibria, one four-phase invariant transformation equilibrium, and five three-phase invariant eutectic equilibria are found.

The maximum temperature on the surface of the liquidus in the system studied is 2440 ℃ and it corresponds to the melting point of Y_2O_3 compound. The minimum temperature on the surface of the liquidus in the system is 1550 °C and it corresponds to three-phase eutectic β-Al_2TiO_5+TiO_2+$Y_2Ti_2O_5$ (E_6) melting temperature.

Since the interaction in the triple system has a mainly eutectic nature, it allows to obtain high-temperature structural composite materials on the basis of directional subtractions of two-phase and three-phase eutectics, in particular for the
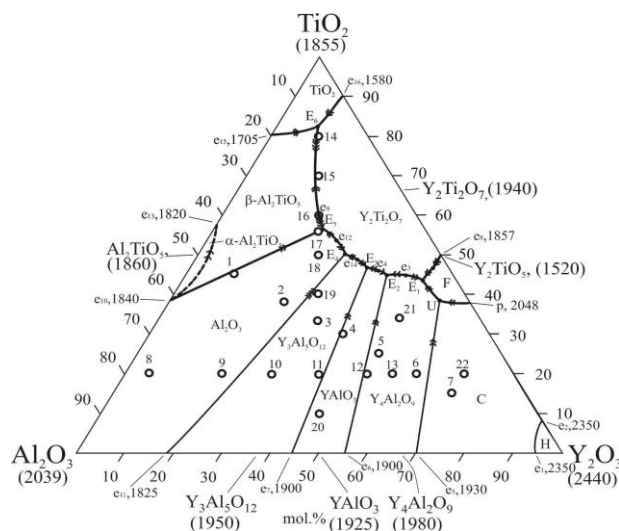
Pig. Liquidus projection of the phase diagram of the Al_2O_3−TiO_2−Y_2O_3 system.

development of refractory ceramic materials.

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THERMODYNAMIC EVALUATION OF INTERACTION OF METALS OF VI-V GROUP AND THEIR COMPOUNDS WITH COMPONENTS OF TUNGSTEN-CARBONATE MELTS

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Oxygen-containing compounds of boron, car-bon, phosphorus, and sulfur, as well as chromium, molybdenum, and tungsten oxides, have been chosen to change the acid-base properties of tung-state melts. On the one hand, these compounds act as donors or acceptors of oxygen ions, and, by changing the basicity of the tungstate melts, facili-tate or hamper the electrodeposition of tungsten. On the other hand, they can be used as sources of the second component in the synthesis of borides, carbides, and sulfides of group VI-B metals, for alloys and intermetallic compounds production.

The probability of the possible reactions of the interaction between the group VI-B metals, their oxides, carbides, tungstates, and oxygen-contai-ning compounds of boron, carbon, phosphorus, and sulfur was estimated on the basis of calculations of the change in the standard Gibbs energy (ΔG_T).

Of the group of boron-containing oxygen com-pounds, sodium metaborate should not be expected to interact with tungstate melt. When the tungstate melt interacts with boron (III) oxide, the reaction will preferably proceed with the formation of di-tungstate ions. Of the group of phosphorus-contai-ning oxygen compounds, sodium orthophosphate should not react with tungstate melt. When the phosphorus (V) oxide and sodium metaphosphate interact with the tungstate melt, the reaction will probably also proceed with the formation of di-tungstate ions. Of the group of sulfur-containing oxygen compounds, sodium sulfate should not be expected to interact with tungstate melt. The reactions of the interaction of lithium and sodium carbonates, and of carbon dioxide, with tungstate melts have $\Box G_t \gg 0$. Oxides of chromium (VI), molybdenum (VI), and tungsten (VI) will interact with these melts to form dimeric compounds.

To identify the refractory metal compounds in sodium tungstate melts containing various oxygen ion donors and acceptors, the IR spectra and the X-ray patterns of the cooled samples were compared with the spectra and X-ray diffraction patterns of pure substances. As the latter, melts were used of chemically pure chromates, molybdates, and tung-states. Melts of dichromates, dimolybdates, and di-tungstates were obtained by sintering of chromates, molybdates, and tungstates with respective metals (VI) oxides. As a result, it was confirmed that dimeric particles could be formed when oxygen acceptors are added to the sodium tungstate melt.

Calculations have shown that group VI-B metals can interact with tungstate-molybdate-carbonate melts with a high probability. The preferred form of existence of chromium, molybdenum, and tung-sten ions in the melt is their dimeric complexes. The interaction of group VI-B metals oxides with these melts is less possible. Group VI-B metals and their oxides will not apparently interact with their dimeric forms ($\Delta G > 0$). Carbides of molybdenum and tungsten can interact with carbonate melts with a high probability, and with ditungstate-dimolyb-date-carbonate melts – with much lesser probability.

From the dependencies of the equilibrium poten-tial of the oxygen electrode on oxygen-containing compounds concentrations, it follows that its value shifts to the positive region when B_2O_3, $Na_2B_4O_7$, P_2O_5, $NaPO_3$, $Na_4P_2O_7$, or $Na_2S_2O_7$ additives are added to the tungstate melt, and to the negative one with the addition of $NaBO_2$, Na_3PO_4, Na_2SO_4, Na_2CO_3, or Li_2CO_3. Thus, the first group of com-pounds acts as oxygen ions acceptors, and the second – as donors.

THERMODYNAMICS OF MOLTEN ELECTROCHEMICAL SYSTEMS WITH ELECTRODES MADE FROM GROUP VI-B METALS AND THEIR CARBIDES

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For the theory and practice of electrodeposition of metals and nonmetals from melts, as well as of synthesis of compounds based on them, important issues are the ability of electrodes and cathode products not to corrode in melts in which their electrodeposition is carried out and existence of equilibrium potentials of the respective electrode or cathode product.

It is these circumstances which determine the possibility of deposition of metals and non-metals onto a particular substrate, the choice of structural materials, the possibility of alloys deposition and the electrochemical synthesis of compounds, the delineation of the regions for various electrolysis products. They have great importance for studying the crystallization overvoltage and for the deposits structure control. Depending on the electrolysis conditions (melts composition, temperature, cathode current density) of tungstate-molybdate-carbonate systems, cathode products can be molybdenum, tungsten, their alloys, oxides, and carbides.

When a reversible process takes place under isothermal conditions with constant pressure, the change in the Gibbs energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are interrelated: $\Delta G = \Delta H - T\Delta S$. It is known that $\Delta S = \left(\partial \Delta G / \partial T\right)_p$, then the Gibbs-Helmholtz equation is valid:

$$\Delta G = \Delta H + T\left(\partial \Delta G / \partial T\right)_p.$$

The free Gibbs energy decrease of the electro-chemical system is equal to the maximum work ΔA which the system can perform, and this maximum work is equal to the product of the sys-tem voltage and the amount of electricity passed, i.e. ZFE: $-\Delta G = \Delta A = ZFE$.

The electrical work done by the system can be greater, less than, or equal to the enthalpy change, depending on the sign of the temperature voltage coefficient.

As examples of electrochemical systems with molten electrolytes, we consider reversible systems with electrodes of group VI-B metals and their carbides:

$$Mo|Na_2WO_4\text{-}MoO_3||Na_2WO_4\text{-}0,2WO_3|O_2,Pt \quad (1)$$
$$MoO_2|Na_2WO_4\text{-}MoO_3||Na_2WO_4\text{-}0,2WO_3|O_2,Pt \quad (2)$$
$$W|Na_2WO_4\text{-}WO_3||Na_2WO_4\text{-}0,2WO_3|O_2,Pt \quad (3)$$
$$WO_2|Na_2WO_4\text{-}WO_3||Na_2WO_4\text{-}0,2WO_3|O_2,Pt \quad (4)$$
$$Cr_2O_3|Na_2WO_4\text{-}CrO_3||Na_2WO_4\text{-}0,2WO_3|O_2,Pt \quad (5)$$
$$Cr_2O_3|NaCl\text{-}Na_3AlF_6\text{-}K_2CrO_4||NaCl\text{-}K_2CrO_4|O_2,Pt(6)$$
$$Mo|NaCl\text{-}Na_3AlF_6\text{-}Na_2MoO_4||NaCl\text{-}Na_2MoO_4|O_2,Pt \quad (7)$$
$$W|NaCl\text{-}Na_3AlF_6\text{-}Na_2WO_4||NaCl\text{-}Na_2WO_4|O_2,Pt(8)$$
$$Mo_2C|Na_2WO_4\text{-}MoO_3\text{-}Li_2CO_3||Na_2WO_4\text{-}0,2WO_3|O_2,Pt \quad (9)$$
$$WC|Na_2WO_4\text{-}WO_3\text{-}CO_2|O_2,Pt \quad (10)$$
$$WC|Na_2WO_4\text{-}WO_3\text{-}CO_2||Na_2WO_4\text{-}0,2WO_3 \quad (11)$$
$$Mo_2C|Na_2WO_4\text{-}MoO_3\text{-}Li_2CO_3||Na_2WO_4\text{-}0,05MoO_3|Mo \quad (12)$$

Reversibility of electrochemical reactions on the corresponding metal and carbide electrodes is beyond doubt.

Systems (1, 3, 6-10) have a negative temperature coefficient, and reactions in them proceed with enthalpy decrease (exothermically). The electrical work which these systems can perform is less than ☐H. Calculations give values of the systems enthal-py changes very close to those determined from thermochemical measurements. In the system (1), 88.5% of the heat produced is consumed to per-form electrical work and 11.5% dissipates or heats the system. In systems (3, 6-10), 84.8; 38.3; 26.4; 30.9; 92.0, and 60.2% of the heat produced are transformed into electrical work, respectively. The temperature voltage coefficients of the systems (2, 4, 5, 11) and (12) are positive. In accordance with this, not only all the heat released during the reaction, but also a part of the heat absorbed from the environment, are transformed into electrical work. The enthalpy values determined from elec-trochemical and thermochemical measurements are in good agreement with each other. Their corres-pondence is one of the criteria for the reversibility of the electrochemical systems under investigation.

FEATURES OF STRUCTURE FORMATION AFTER THERMAL SYNTHESIS OF COMPOSITE MATERIALS *BASED* ON TiH$_2$-Si-C SYSTEM

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In recent years, MAX phase – materials based on layered structures of ternary compounds, has attracted much interest. It's general formula *Mn+1AXn* (*n* = 1÷3), where M is a transition *d*-metal, A is an *p*-group element (e.g. Si, Ge, Al, S, Sn and oth.), and X is either carbon or nitrogen [1-2].

The most promising for practical use are materials based on the most fully studied - Ti$_2$AlC, and especially Ti$_3$SiC$_2$ MAX phases.

Titanium hydride, semiconductor silicon and technical carbon powders were used as starting materials.

It is known [3] that use of titanium hydride powders activates of diffusion upon sintering and accelerates phase formation during synthesis. The initial powders were mixed in a molar ratio of 3:1:2 components in a "drum tumbler" within 2 hours. The powder mixtures were subjected to two-way cold pressing (400 MPa), which subsequently were sintered in vacuum furnace at temperature 1150, 1300 and 1400 ^{0}C with isothermal holding of 60 minutes.

Samples are sufficiently strong spongy conglomerates after thermal synthesis, reminiscent of the ones obtained by the SHS methods.

There are 3 structural components are observed in the structure of the samples synthesized at 1150 ^{0}C (Fig. a): dark, light gray and spherical particles. Dark inclusions are free carbon particles that have not reacted during the synthesis process. A light gray background field can be identified as a titanium silicide Ti$_5$Si$_3$ [2]. The main carbide phase is presented as homogeneous dispersion of titanium monocarbide particles close to the spherical form with an average grain size of 1÷3 μm.

Increasing the sintering temperature to 1300 ^{0}C (Fig. b) accompanied by a significant change in the phase composition. The structure becomes more coarsely dispersed, the average grain size increases to 5÷7 μm. A small amount of laminate-like grains of the ternary Ti$_3$SiC$_2$ compound is formed in the structure, the amount of which substantially increases with increasing synthesis temperature to 1400 ^{0}C (Fig. c). Also Increasing the sintering temperature leads to crystals growing to 5÷7 μm in the section and 15÷20 μm along the length.

a

b

c
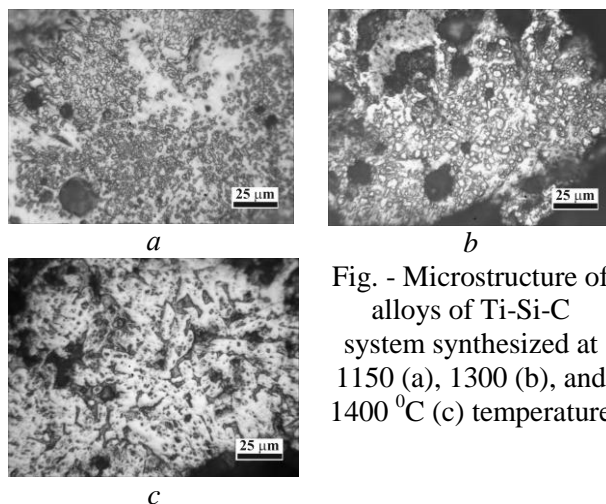
Fig. - Microstructure of alloys of Ti-Si-C system synthesized at 1150 (a), 1300 (b), and 1400 ^{0}C (c) temperature

From these arguments conclude that increasing the sintering temperature affects the structure of material and leads to a significant change in the constituents of the alloy. In the alloy synthesized at 1150 ^{0}C, the leading phase is titanium monocarbide TiC, while at 1400 ^{0}C the main phase is Ti$_3$SiC$_2$.

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PECULIARITIES OF FORMATION OF PHASE COMPOSITION AND PHYSICO-MECHANICAL PROPERTIES OF HOT-SPREADED CERAMICS B_4C-CrB_2-TiB_2

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This work is devoted to the study of the formation of the structure and properties of ceramic materials of polyfunctional use based on boron carbide.

Previous studies [1],[2] have shown that in B_4C-MeB_2 ceramics obtained by the method of reaction hot pressing, anomalous grain growth can be eliminated and a fine-grained structure with a high level of mechanical properties can be eliminated in the extended interval, compared with monophasic boron carbide hot pressing temperatures.

The results of studying the hot pressing process and the properties of B_4C-CrB_2-TiB_2 ceramics are presented.

It has been established that the simultaneous introduction of relatively small amounts of chromium (Cr_2O_3) and titanium (TiO_2) oxides into the boron carbide charge containing free carbon makes it possible to obtain a dense, highly disperse composite ceramic of the B_4C-CrB_2-TiB_2 system with a homogeneous structure during the reaction sintering.Phase analysis (Fig. 1) showed that in this ceramic there are:
1) boron carbide;2) graphite;
3) TiB_2 solid solution of Cr;
4) Cr_5B_3 solid solution of Ti.

The sintering process takes place at a lower temperature of isothermal aging.

In composite ceramics, with the content of chromium boride and titanium boride up to 10 volume%, the improvement in strength properties is explained by the mechanism of enveloping obstacles by propagating cracks. Such composite ceramics have higher values of hardness and bending strength than single-phase ceramics based on boron carbide.
Elastic characteristics also have high values [2] and determined by the composition of the ceramics. The introduction of these oxides makes it possible to use cheaper powders of boron carbide with a high content of free carbon.

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2. Grigoriev O., Kovalchuk V., Bega N., Galanov B., Kotenko V., Zaporozhets O., Kutran T., Dordienko M. Obtaining and physico-mechanical properties of B4C-VB2 composites // Powder metallurgy.-2006.-No.1 / 2.- P. 59-72.

1 - Boron carbide; 2 - Graphite; 3 - TiB_2 (Cr); 4 - Cr_5B_3 (Ti)
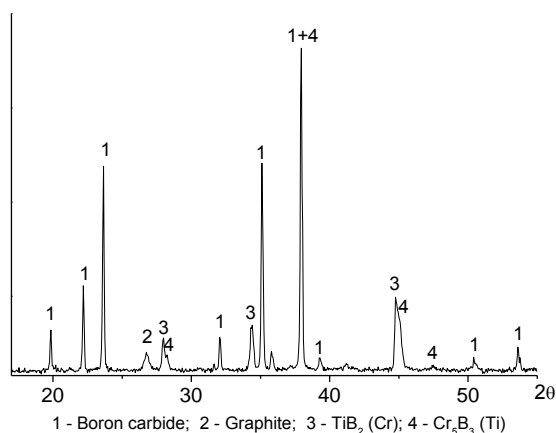
Fig.1.Diffractogram of hot-pressed ceramics B_4C + 5 wt% TiO_2 + 2 wt% Cr_2O_3

INFLUENCE OF SINTERING TEMPERATURE ON THE STRUCTURE AND PROPERTIES OF WEAK-RESISTANT POWDER MATERIALS OF THE FE-FH800 SYSTEM

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One of the perspective powder materials for work in conditions of friction, abrasive wear and elevated temperatures is carbidechrome alloys with a binder on the iron base of the KHZH series. It is also wear-resistant materials such as iron - ferrochromium.

The studies were carried out on charge materials based on iron with additives of high-carbon ferrochromium (35 wt.%). Powder of high-carbon (8.6% wt.% C) ferrochromium was obtained by mechanical grinding of lump material. The iron powder of PZHR 3.260.28 as an initial metal component was used.

The influence of the sintering temperature on the properties of materials in order to determine the optimum conditions for obtaining materials of the Fe-Cr-C system for samples was investigated.

Dependences on the sintering temperature of density, porosity, and volume shrinkage of the samples obtained at temperatures of 1150 °C, 1200 °C, 1250 °C and 1300 °C were studied at an isothermal holding time of 30 min. The increasing of sintering temperature leads to an increasing of density of the samples and their greater shrinkage. This is due to the thermal activation of diffusion processes, which underlie all operating sintering mechanisms.

Investigation of the microstructure of sintered samples showed that it is a steel matrix in which the inclusions of the solid phase are distributed.. The average grain size of the carbide phase is about 6 μm, the metal phase is 19 μm. The average size of carbide metal grains increases by a factor of 1.5 with an increasing of sintering temperature from 1150 to 1300 °C. The material structure is heterogeneous and consists of solid grains of complex iron chromium carbide uniformly distributed among the elastically plastic metal matrixand it is α-Fe.

Thus, the results of the study indicates that with an increasing of sintering temperature from 1150-1300 °C the structure of the material varies from three phase to multiphase.

a   *b*

c   *d*
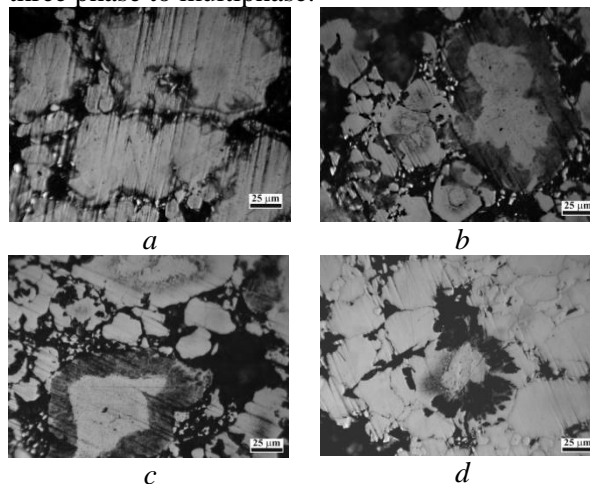
Fig.1 - Micro-X-ray spectral analysis of samples of Fe - (35% wt) FX800 powder sintered at temperatures of 1150 °C (a), 1200 °C (b), 1250°C (c), 1300°C (d)

The results of micro-X-ray spectral analysis showed that the main phase of the samples at low temperature is the iron-based phase (Fe-99.3%, Cr-0.73%, C-0.13%), and the carbides are M3C (Fe-24.6 %, Cr - 68.4%, C - 7.06%). Carbides were converted to M_3C_2 (Fe-22.5%, Cr-64.24%, C-13.25%) starting with the sintering temperature 1200-1300 °C.

Optimum conditions for sintering (Tsint-1250 °C, τ-30 min.) of Fe-FH800 powdered materials and the changes in their phase composition as a function of the sintering temperature are established.

Using the micro-X-ray spectral analysis, it was shown that with an increasing of the sintering temperature from 1150 to 1300 °C the composition of carbides varies from M_3C to M_3C_2.

REACTION-SINTERED SILICON CARBIDE MODIFIED BY CHROME CARBIDE

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The aim of the paper is to study the regularities of the formation of SiC in the processes of impregnation of porous preforms containing silicon carbide, carbon and dispersed chromium carbide as a modifier in liquid silicon. As initial components, a nanosized silicon carbide powder was used [1, 2], an industrial silicon carbide powder with a particle size of 28 μm, and synthesized chromium carbide (Cr_3C_2) [3]. Impregnation of samples with silicon was carried out in an induction furnace at a temperature of 1950 °C in argon.

It is established that the structure of the reaction-sintered silicon carbide (RSSC) depends on the structural features of the initial components. When industrial powder is used for the hexagonal structure of silicon carbide with a particle size of 28 μm, the structural state does not change, since the formed secondary 3C-SiC is converted to the same hexagonal 6H-SiC. As can be seen from Table 1, the use of nanoscale silicon carbide of cubic modification (3C-SiC) leads to the formation of a small hexagonal 6H-SiC structure during the formation of the structure of the RSSC.

Table 1. Phase composition of RSSC samples of modified 5% chromium carbide

Particle size SiC	Phase content, %		
	Si	6H-SiC	3C–SiC
nano	10,6	4,8	84,6
28, мкм	7	93	–

The obtained non-porous preforms of RSSC were investigated by electron microscopic analysis (Fig. 1).

a – SiC28μm   *b* – nanoSiC
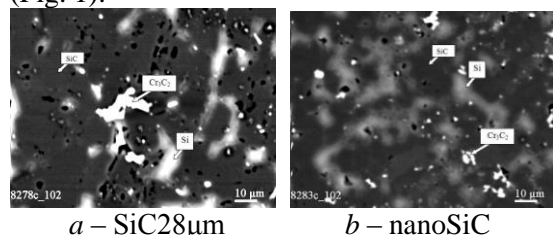
Figure 1 - Fragments of microstructures of RSSC modified with 5% chromium carbide

The dark areas on the images are identified with the phase of silicon carbide, light - with free silicon, and the brightest - with chromium carbide.

Analysis of the images of various sections of the structure of the RSSC in the characteristic rays of chromium showed that chromium carbide is localized in the regions of free silicon (Fig. 2).

a – SiC28μm   *б* – nanoSiC
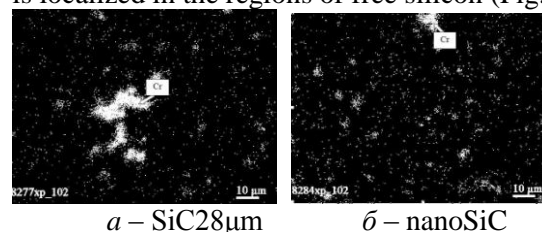
Figure 2 - Image of fragments of microstructures of RSSC modified with 5% chromium carbide in characteristic rays of chromium

Thus, the use of a hexagonal structure of silicon carbide with a particle size of 28 μm does not change its structural state when modified with chromium carbide. The use of nanoscale silicon carbide of the cubic modification results in the formation of the structure of the RSSC in the process of stabilization of the cubic 3C-SiC structure and the insignificant appearance of the hexagonal 6H structure.

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COMPOSITES BASED ON IRON MODIFIED WITH SYNTHESIZED POWDER LIGATURE IN THE SiC–Fe$_2$O$_3$ SYSTEM

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The aim of the work is to study the structure of metallic composite materials based on iron at using a synthesized finely dispersed powder product in the SiC–Fe$_2$O$_3$ system as the ligature, and to study their mechanical characteristics.

The starting components were iron powder of the brand PZR4 and synthesized powder (ligature) formed by the interaction of nanosized powder of nonstoichiometric silicon carbide (SiC-C) [1] with iron oxide pigment (α-Fe$_2$O$_3$) (as per TU 6-10-2029-86). The powder of ligature contains silicon carbide, iron silicides and silicon oxynitride phases [2]. Fusion of the Fe – ligature system of powder mixtures was carried out in an induction furnace at 1700° C for 40 minutes.

It is established that the highest strength and plasticity has the sample with 3 mass.% the ligature content.

Table. Mechanical characteristics of Fe-based composites formed with the participation of a ligature synthesized in the SiC–Fe$_2$O$_3$ system

Ligature content, mass.%	$\sigma_{0,2}^{\tilde{n}}$, MPa	$\sigma_{\tilde{A}}^{\tilde{n}}$, MPa	ε, %	HV 0,2, GPa
3	1237	1898	29,1	4,4
5	1218	1871	26,8	4,4
7	928	1494	16,8	4,9
22H2G2R	980	1230	6,0	–

22H2G2R – industrial structural low-alloy steel (armature of class A1000)

It is demonstrated that the formed composites surpass the industrial structural low-alloy steel grade 22H2G2R by 28% in strength and almost 5 times in plasticity.

It is established that metallic composites have a highly dispersed pearlite structure. The thickness of the plate formations of iron carbide is 20–25 nm with a distance between them up to 150 nm.
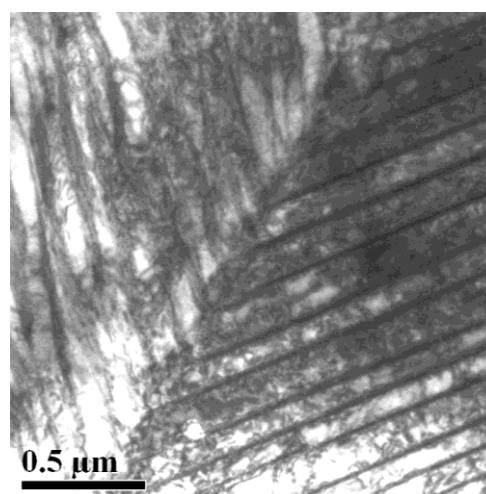
Figure. Microstructure of Fe-based composites formed with the participation of a ligature synthesized in the SiC–Fe$_2$O$_3$ system

Thus, metal composites modified with synthesized powder ligature in the SiC–Fe$_2$O$_3$ system are characterized by increased strength characteristics due to the formation of a nanosized pearlite structure.

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CORROSION RESISTANCE AND INERTNESS OF REFRACTORY MATERIALS ON BASE OF HALOGENIDES AND CRUCIBLE REUSABLE OF THEM FOR SYNTHESIS, CASTING AND HOMOGENIZATION OF ALLOYS WITH Ti, Zr, Hf, V, Nb LARGE CONTENTS.

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Ti, Zr, Hf, V, Nb and them alloys are used, as the braze alloys for brazing different ceramic materials, and, as amorphous metal materials (many-component systems on base Zr and/or Ti), which due to a complex of unique physic-chemical properties are used in different industries.

Synthesis is by one of methods of receipt of alloys in ceramic crucibles. However isothermal melting and homogenisation of such alloys were impossible. For following reasons Ti, Zr-containing alloys have high activity in a contact to the majority of standard refractory on the basis of refractory oxides, carbides, and also they wet these refractories. Concerning large amount of Ti, Zr, Hf (up to 20–30 mass %) in alloys destroys the crucibles.

The anomalous phenomenon – non-wetting at high temperatures (table) and abnormal inertness effect of fluorides to contact with aggressive alloys with large contents of Ti, Zr, V, Nb have been established. It allows, to use refractory fluorides as refractory for manufacturing products from them (crucibles, cups), which can be used for melting and homogenization of chemically aggressive alloys.

Table. Wetting results of fluorides by metal melts

Subst.	Melt	T, ˚C	θ, deg.
SrF_2	Cu + 50 mass % Ti	1200	119
- " -	Cu + 50 mass % Zr	1200	110
- " -	Ni + 70 mass % Ti	1200	114
- " -	Ni + 70 mass % Zr	1250	119
CaF_2	Cu + 50 mass % Ti	1200	116
- " -	Cu + 50 mass % Zr	1200	108
- " -	Ni + 70 mass % Ti	1200	111
- " -	Ni + 70 mass % Zr	1250	124
- " -	Ni + 80 mass % Hf	1250	118

The powder metallurgical techniques make crucibles, cups and forms for a casting, melting and homogenization of high chemically active alloys.

Crucibles and cups for isothermal synthesis and homogenization of chemically active alloys with the contents (up to 80 mass %) Ti, Zr, Hf, V, Nb by methods of powder metallurgy (pressing and sintering) were received. Crucibles have the diameter up to 50 mm and height up to 100 mm and the porosity about 20-40 %.

At melting of such alloys in fluoride crucibles has been established, that due to the big differences in factors of temperature expansion (α) (for CaF_2 $\alpha=18,5 \cdot 10^{-6}$ 1/K), and for Ti, Nb, V, Sn, Cu, accordingly, α it is equaled 8,3·10-6, 7,1·10^{-6}, 9,6·10^{-6}, 23·10^{-6}, 16,6·10^{-6} 1/K) a mechanical compression of an alloy, which is cooled, in crucible occurs. It results to destruction of the crucibles. To resist to such phenomenon and taking in attention the wetting of fluorides by such alloys (the big contact angles) we have suggested to use for melting and homogenization of such alloys the crucibles, which are disassembled. The crucible will consist of several parts (fig. 1). Such crucibles it is possible to use a plenty of times.
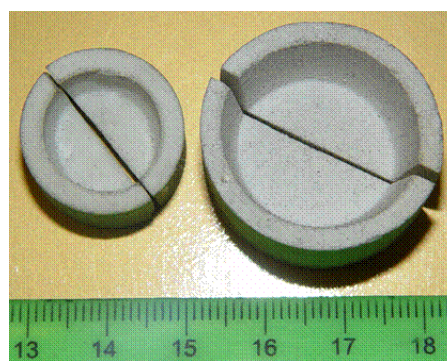
Fig. 1. Crucible reusable.

Fluoride refractory and products from them (crucibles, cups, crucible reusable) can be used for synthesis and homogenization of amorphous metal alloys, of alloys with memory effect of the form, of brazing alloys with Ti, Zr, Hf, V, Nb.

PHASE COMPOSITION STUDY OF DYSPROSIUM TITANATE PREPARED BY THE CHEMICAL PRECIPITATION METHOD AFTER ANNEALING AT 600…1650 □C

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Dysprosium titanate is used as an absorption material for the control assemblies of the nuclear reactors.

Nowadays the main methods of industrial production of dysprosium titanate are: solid state synthesis (realized by high-temperature heating of dysprosium and titanium oxides mixture) and method of induction melting in a cold crucible.

In recent years research and activities in the field of low-temperature synthesis of dysprosium based complex oxygen compounds have intensified. The most wide spread among them are: mechanochemical synthesis in high-energy planetary mills, methods based on the decomposition of salts and high molecular organic polymers, methods of chemical precipitation of hydroxides from salt solutions with subsequent annealing. These methods allows to obtain sub microcrystalline and nanocrystalline dysprosium titanate powders. This article represents the XRD analysis results of products of thermal decomposition of co-precipitated dysprosium titanate hydroxide in the temperature range of 100….1650 °C.

It is shown that precipitated product is amorphous. An increase of the calcination temperature of hydroxides up to 600 °C causes the crystallization of orthorhombic modification of dysprosium titanate Dy_2TiO_5-o and pyrochlore-type $Dy_2Ti_2O_7$ titanate. At this temperature the crystallite size is 70…90 nm. As the calcination temperature increases up to 1100 °C, the growth of crystallites is observed and the formation of rigid agglomerates of the adherent submicron particles take place.

Subsequent mechanical activation, powder molding and sintering at T=1650 °C for 3 hours provides to obtain two-phase tablets density of 6.6 g/cm^3, which consists of pyrochlore $Dy_2Ti_2O_7$-pand fluoriteDy_2TiO_5-f.

PRODUCTION AND CHARACTERISTICS OF CERAMICS FROM NANO-DIMENSIONAL ZIRCONIUM OXIDE POWDER

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In view of the significant variety of properties, ceramics based on zirconium dioxide (ZrO_2) occupies a special place in the list of promising materials, interest in which is becoming ever more extensive. The development of methods for obtaining ZrO_2 nanopowders with controlled characteristics, methods for their compacting and sintering of specimens with the required physicomechanical characteristics is being actively pursued. Due to its high biocapacity, ZrO_2 can be used in medicine. Also, zirconium oxide is currently used to develop radiation-resistant matrices for the immobilization of radioactive waste (RW). This paper presents the results of studies of the phase composition, microstructure, and some characteristics of the initial ZrO_2 powder of a stabilized 3% mole of Y_2O_3 grade PSZ-5,3YV produced by Stanford Materials Corporation (USA).

It is established that the initial powder is biphasic. The monoclinic modification (ZrO_2-m) content was 54.9%wt and the tetragonal modification (ZrO_2-t) - 45.1%wt. The size of the coherent scattering (OCD) regions of the first and second phases is 36.6 nm and 40.6 nm, respectively. The density of the samples sintered at 1450 °C was (5.6...5.7) g/cm^3. Samples sintered at 1550 °C and 1650 °C had a density (5.9...6.03) g/cm^3. It was found that with an increase in the sintering temperature there is an increase in the grain size. So the average grain size of samples sintered at 1450 ºC, 1550 ºC and 1650 ºC, was 319±21 nm, 581±64 nm and 967±67 nm respectively. Samples sintered under these conditions are also two-phase, the main structural constituent is a cubic modification (ZrO_2-c) with a concentration

(85...88)%wt. The second phase is tetragonal ZrO_2. The external appearance of the initial powder and the microstructure of the sample sintered at 1550 °C, 3 hours are shown in Fig. 1.
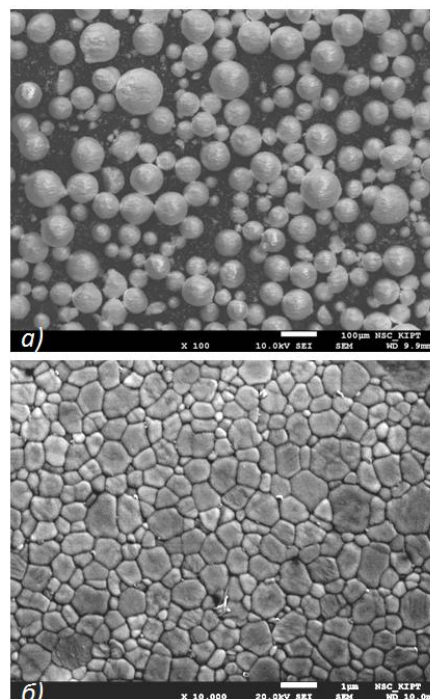
Fig. 1 - Appearance of ZrO_2 powder (a) and microstructure of the sintered sample (b)

In the course of the work, optimal regimes for the preparation of ceramics based on ZrO_2 (3% Y_2O_3) were established, which amounted to a sintering temperature of 1550 °C and a holding time of 3 hours. It is shown that the obtained ceramic has a high density (98.2% TD) and is characterized by a homogeneous and fine-grained structure (581±64 nm).

ADJUSTMENT OF CATHODE DEPOSITS COMPOSITION IN TUNGSTEN-MOLYBDATE MELTS

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It was established earlier that refractory metals, their dioxides, and compounds with alkali metals and oxygen of different composition (bronzes) can be deposited from the Me_2MO_4-MO_3 melts (where Me is Li, Na, or K, and M is Mo or W). However, concentration and temperature ranges for these products obtaining were not determined practically or required refinement.

1. The Li_2WO_4-WO_3 system. The effect of WO_3 concentration in lithium tungstate melt was studied within the range $0 \div 80$ mol. %. As the content of WO_3 in the melt increases, the content of lithium in bronze decreases. At low concentrations of tungsten anhydride (up to 10 mol.%), electrodeposition of tungsten oxide (IV) occurs.

An increase in the electrolysis temperature within the interval $1123 \div 1273$ K, with the same electrolyte composition and current density $5 \cdot 10^{-2}$ A/cm^2 leads to an insignificant crystals enlargement and an increase in the lithium content in bronzes.

With WO_3 concentration below 40 mol.% and with the electrolysis temperature increase, metallic tungsten begins to deposit. At the same time, the lower the WO_3 concentration, the lower the temperature at which the metal begins to deposit. With WO_3 concentrations above 40 mol.%, tungsten (IV) oxide or bronze are deposited.

2. The Na_2WO_4-WO_3 system. From the diagram of the products composition of this system electrolysis, it can be seen that the area of bronzes deposition in it is much wider than for the Li_2WO_4-WO_3 system, and shifted towards lower WO_3 concentrations. The region of the metallic tungsten deposition is shifted toward low temperatures and high WO_3 concentrations. As in the case of the molten Li_2WO_4-WO_3 system, during the electrolysis of molten Na_2WO_4-WO_3 system, deeper reduction of tungsten is observed with WO_3 concentration decrease in the melt. The sodium content in bronze is increased. However, at x > 0.93, sodium-tungsten bronzes of Na_xWO_3 composition are unstable due to the strong compression of the crystal lattice. Therefore, during the electrolysis of Na_2WO_4-WO_3 (< 40 mol. %) system, the ditungstate ions are reduced not to bronzes, but to dioxide WO_2.

3. The K_2WO_4-WO_3 system. As in Li_2WO_4-WO_3 and Na_2WO_4-WO systems, a deeper reduction of cathode products is achieved with the WO_3 content decrease and the electrolysis temperature increase. The range of compositions of potassium-tungsten bronzes K_xWO_3 is limited to x < 0.6. Therefore, with WO_3 < 30 mol. %, bronzes are not formed at all. In contrast to the previous systems, the WO_2 is not deposited at the cathode. Instead, within all investigated temperature intervals, metallic tungsten is deposited.

4. The Me_2MO_4-MoO_3 systems. We've studied the effect of the molybdenum (VI) oxide concentration and of the melt cationic composition on the composition of cathode deposits. The experiments were carried out in Me_2WO_4 melts (where Me - Li, Na, K, or Rb) at 1173 K and with cathode current density 0.05 A/cm^2. It was found that, with high MoO_3 concentrations in the melt, molybdenum (IV) oxide is deposited at the cathode instead of the metal. The boundary concentration at which this occurs increases from 2.0 up to 8.5 mol.% during the transition from Li_2WO_4 to Na_2WO_4, K_2WO_4, or Rb_2WO_4 (i.e. with increase of the alkali metal cation radius).

5. The Na_2MoO_4-MoO_3 and Na_2MoO_4-Na_2WO_4-MoO_3 systems. Unlike the systems described above, in molybdate melts there is no molybdenum electrodeposition. As it can be seen from the composition diagram of the products, molybdenum dioxide deposites on the cathode within a wide range of melts compositions. The area of sodium-molybdenum bronzes deposition is not large. The above features are also characteristic for melts of the Li_2MoO_4-MoO_3 and K_2MoO_4-MoO_3 systems.

TWO-LAYER PCBN COMPOSITES FOR USE IN A TOOL

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There are two types of cutting inserts: disposable (single-layered) and two-layered plates with a cBN layer on a carbide substrate in the nomenclature of tool materials based on cubic boron nitride (cBN) from world famous companies in South Africa, the United States, Japan, China. The diameter of two-layered plates is up to 50.8 mm, the total thickness is up to 6.35 mm, the thickness of the cBN layer is up to 1.6 mm. The carbide substrate plates are usuallysubject to laser cut for produce blanks, from which, with the help of soldering, with subsequent cutter grinding, tools of a complex profile are made. The scientific and technological base for design and production at high pressures of super-hard PCBN plates, consisting of a working layer based on cBN and a hard-alloy substrate, was created in the ISM. Samples were obtained by charge sintering in high-pressure apparatus (HPA).

In this paper, we present the results of studying the structure and properties of PCBN composites produced by reactive sintering under high pressure (4.2 GPa) and temperature (1750 K) powders of cBN with Al, Ti, Co and Ni on a VK15 hard alloy substrate. High-pressure apparatuses «anvil with recess» were used. The obtained samples after mechanical treatment with a free and bound abrasive had dimensions of 12.7 mm in diameter and 4.8 mm in height. The phase composition was determined by X-ray diffraction analysis (DRON-3, CuKα-radiation). The hardness was determined on the PMT-3 device using the Knoop pyramid, the load on the indenter is 10 N, the electric resistivity is measured using a digital ohmmeter «Щ-34», whose measuring range is 10^{-3}-10^{9} Ohm. The cutters working capacity of two-layered superhard composites was investigated on an automated stand based on a turning machine 1К62 at the final turning of ХВГ steel HRC58-60. A cutter with a mechanical fastening of a circular PCBN cutting plate with a diameter of 12.7 mm had geometrical parameters: the front angle γ = -10 °; the relief angle α = 10 °. Cutting speed v, cutting depth t and advance S were 1.5 m/c, 0.02 mm and 0.07 mm/vol. respectively.

Hardness and electrical resistivity test results of two-layered PCBN composites of systems cBN-Me-Al, (Me-Ni, Co, Ti) obtained by reaction sintering at a pressure of 4.2 GPa and a temperature of 1750 K in the HPA «anvil with recess» are given in table.As can be seen from the table, the highest hardness is in the cBN-Al composite, the decrease of the cBN content in the charge leads to decrease composite hardness. The lowest electrical resistivity is in cBN-Ti-Al composites, the difference is 2-3 orders. The lowest wear in the composites of the cBN-Ti-Al system is for the case of 10%massTi in the charge, as the proportion of titanium in the charge increases, the wear of the composite increases. It should be noted that for single-layered composites of the same systems the properties are different: hardness is higher by 5-10%, electrical resistivity is 3-5 times higher, wear is lower by 15-20%. The main reason of the difference properties of the working layer of a two-layered plate from a single-layered composite obtained with the same charge and with the same sintering parameters is the migration cobalt from the carbide substrate in the composite working layer during sintering.

Table. Properties of two-layered composites cBN-Me-Al, (Me-Ni, Co, Ti) obtained at a pressure of 4.2 GPa and a temperature of 1750 K

№	Charge composition,% mass	Hardness, GPa	Electrical resistance of the working layer, Ohm·m	Wear on the relief surface, h_z, mm
1	90 % cBN, 10 % Al	27,5±1	$1,9 \cdot 10^{-1}$	0,23
2	80 % cBN, 10 % Ti, 10 % Al	26,5±1	$2,2 \cdot 10^{-3}$	0,21
3	67 % cBN, 23 % Ti, 10 % Al	25,0±1	$7,2 \cdot 10^{-4}$	0,25
4	57 % cBN, 33 % Ti, 10 % Al	23,5±1	$3,9 \cdot 10^{-4}$	0,28
5	85 % cBN, 5 % Co, 10 % Al	25,5±1	$8,3 \cdot 10^{-2}$	0,23
6	83 % cBN, 7 % Ni, 10 % Al	26,0±1	$1,1 \cdot 10^{-1}$	0,26

INVESTIGATION OF MAGNETIC CHARACTERISTICS OF SAMPLES THERMOMAGNETIC POWDER MATERIALS IN A CONSTANT MAGNETIC FIELD

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Precision alloys are widely used in electrical and radio engineering, aerospace and nuclear, electronic and instrumentation manufacturing industry, as well as in industries, which generate communication facilities and automated systems, electronic computing machines and microprocessors.

Thermomagnetic alloys manufacturing by means of the powder metallurgy method allows with high prescription accuracy of chemical composition of precision powders of Fe, Ni, Ti, Mo, Cu on the basis of weight measuring to reach homogeneous composition in a solid phase without melting of the material. In future it will allow to record the Curie temperature in the required temperature range with a small acceleration. Investigation of magnetization curves of samples of thermomagnetic powder materials with different Cr contents (Fig.1) showed that the greatest magnetic induction was assigned to samples with 3% Cr. Moreover, there is a tendency towards decrease of the magnetic induction of samples with increase in chromium concentration. It can be explained by the fact that with increase of the concentration of Cr, the time of Ni-Fe-Cr phase increases, which has less inductance.

Meanwhile, the time of iron-based phase with a higher intensity of saturation decreases, which is confirmed by the microstructures of the samples of thermomagnetic powder alloys. Curie temperatures were determined graphically by extrapolating the temperature dependence (B=f(H)) to the temperatures axis. Graphics of thermomagnetic characteristics of samples of powder thermomagnetic alloys (Fig.2) show that an increase in the concentration of chromium leads to a decrease in the Curie temperature of the powder thermomagnetic alloys. It is explained by the fact that with an increase in the concentration of chromium, the rate of formation of a triple solid solution of Ni-Cr-Fe increases, which has the temperature dependence on the magnetic induction.
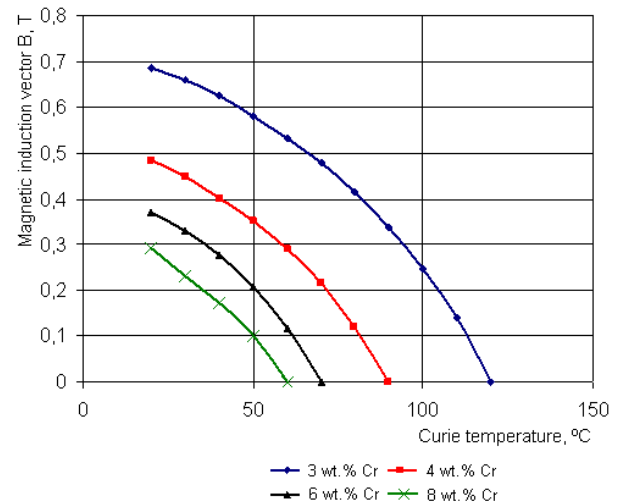
Fig.2 Thermomagnetic characteristics of samples of powder thermomagnetic alloys with a different content of Cr at an intensity of external magnetic field 8000 A/m.

Thereby, the magnetic characteristics of powder thermomagnetic materials, which determine the range of operation temperature-sensitive element in relay constructions, were investigated.

Fig.1 Main magnetization curves of samples of powder thermomagnetic alloys with different chromium content

STUDY THE EFFECT OF ANVIL'S LATERAL SUPPORT PRESSURE OF THE HPA OF THE "ANVIL WITH RECESS" TYPE ON THE GENERATED WORKING PRESSURE

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To create the high pressure and the high temperature required for the synthesis of diamonds, cubic boron nitride and the sintering of polycrystals on their basis, as well as to carry out the other works, high-pressure apparatuses (HPA) of various designs are used [1], including the apparatus of the "anvil with recess" type (HPA AWR). Among the various modifications of HPA AWR, the highest working pressure (up to 7,5 GPa) and temperature (up to 2000 ° C) are achieved using the HPA of the "toroid" type (HPA T) (Fig. 1).
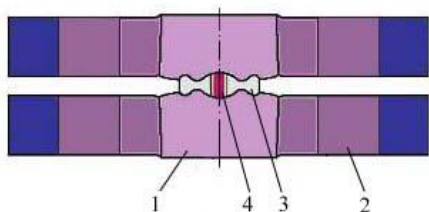
Fig. 1. Scheme of HPA T: 1 – anvil; 2 – block of binding rings; 3 – high pressure cell; 4 – the sample to be studied

One of the prerequisites for achieving of high working pressure in HPA T is the creation of sufficient pressure between the anvil 1 and the block of rings 2 (lateral support pressure for the anvil p).

The aim of this work is to study the effect of the lateral support pressure of the anvil p on the achievable working pressure (p_{max}) in the HPA T.

At the research a special technique based on numerical calculations of the values of equivalent stresses for the third (σ_e^{III}) and fourth (σ_e^{IV}) strength theories with the taking into account the effect of hydrostatic pressure on the strength characteristics of the anvil material ($R_{c0.2}$, etc.) has been used to calculate the necessary (sufficient) lateral support pressure for the HPA T anvil to ensure its operability.

The fragment of the calculation scheme and the distribution of equivalent stresses σ_e^{IV} (GPa) in the anvil from hard alloy HB02UF under the load with working pressure of p_{max}=15 GPa and lateral support pressure of 3,0 GPa are shown in Fig. 2
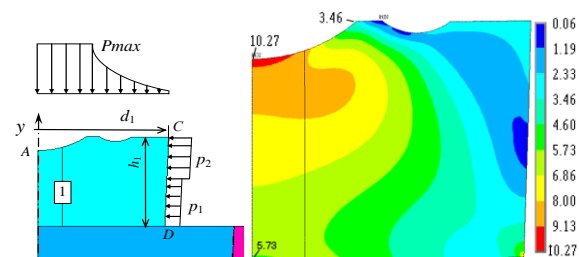
Fig. 2.

As an example, Fig. 3 shows the dependence of the maximum equivalent stress in the anvil, made of high quality hard alloy grades NF ($R_{C0.2} = 8,11$ GPa) and HB02UF ($R_{C0,2} = 6,8$ GPa), on the lateral support pressure at a load of working pressure 15 GPa. The values of the lateral support pressure, which are required to ensure the operability of the anvils, are determined (Fig. 3).
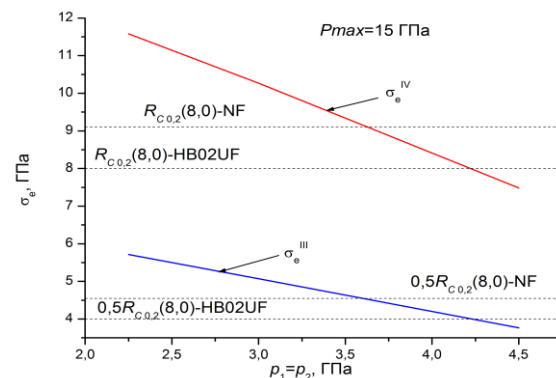
Fig. 3.

As a result of the carried out researches the technique is developed, the possibility and the technical solutions for increasing the pressure in the HPA AWR with an increased pressure of the lateral support of the anvils are justified.

1. *Sverkhtverdye Materialy. Poluchenie i primenenie,* (Superhard materials. Production and applications), 6 vols., Novikov, N.V., Ed., Synthesis of Diamonds and Related Materials, vol. 1, Shul'zhenko, A.A., Ed., Kiev: Bakul' Institute for Superhard Materials, National Academy of Sciences of Ukraine, 2003.

LUMINESCENT PROPERTIES OF FINE-DISPERSED SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIZED ZnS:Cu,Mg

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Luminescent characteristics of light-emitting materials largely depend on the material structure, ratio of impurities acting as luminescence activators and co-activators, etc. Studies of the materials obtained using unconventional methods, such as SHS, are of particular interest. In it was shown improvement of luminescent characteristics in thin-film devices based on ZnS:Cu,Mn after doping MgF2 and MgS. Also, increasing the intensity of photoluminescence (PL) after introduction of MgS or MgCl2 in defined concentration was noted. At the same time, the resistance to degradation of luminophores is a necessary condition for their successful use. The goal of this work was to study the influence of magnesium impurities that were introduced into ZnS as activator and co-activator in fine-dispersed ZnS:Cu obtained using the SHS method, and time evolution of luminescent characteristics of obtained luminophores.

Electron microscopy study of ZnS:Cu,Mg-SHS showed that the synthesized powders consist of two fractions. Fraction consists particles with dimensions1-2 μm.and 10-100 nm.

According to EDS measurements, elemental composition of fine-dispersed ZnS:Cu,Mg-SHS is close to the stoichiometric one.

As can be seen from Fig. in the spectra of undopedZnS-SHS and ZnS:Mg are almost identical by their spectral composition. This means that luminescence of both powders is self-activated and caused by identical centers.

Investigation of composition of ZnS:Cu,Mg-SHS PL spectra, showed a significant difference in comparison with the spectrum of undopedZnS-SHS and ZnS:Mg-SHS.
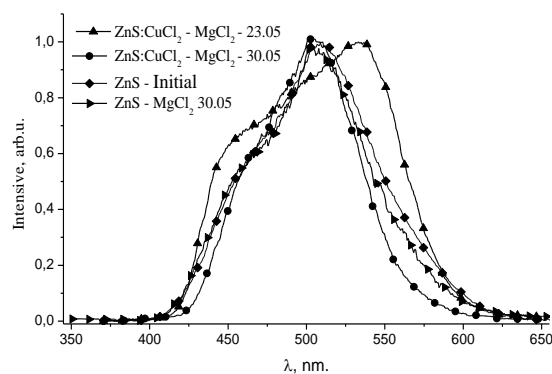
Therefore, at the beginning of introduction of MgCl$_2$ into the charge, magnesium compounds lead to mass transfer between particles of ZnS, i.e. act as a flux. According to, it may contribute to introduction of an activator (copper or some other dopants) into lattice of luminophore. In the further relaxation processes (especially if synthesis conditions facilitate the formation of unstable structural states or phases), presence of magnesium promotes deformation processes, which leads to changes in symmetry of ZnS crystal lattice. It becomes a reason for quenching the PL bands, which is caused by presence of copper impurities.

NEWFIELDOFAPPLICATIONOF PCBN«KIBORIT» - THE FRICTIONWELDINGWITHMIXING

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At V.N. Bakul Institute for Superhard Materials one of the priorities is the development of polycrystalline superhard materials based on cubic boron nitride (PCBN). PCBN materials of the trade mark «Kiborit» [1], occupy a prominent place among the materials of this class. Polycrystals are produced by reactive sintering in an «anvil with recess» high-pressure apparatus (HPA) at a pressure up to 5 GPa and a temperature of up to 2000 K. The obtained products were cylindrical shape with dimensions up to 32 mm in diameter and up to 25 mm in height. The materials have a high hardness (up to 40 GPa), crack resistance (up to 13 MPa·m$^{1/2}$), thermal conductivity (up to 100 W/(m·K)), acid stability in the air (up to 1200 K) and thermostability (up to 1400 K). The main application area of «Kiborit» is a cutting tool for roughing and semifinish machining of high-alloy and stainless steels, special alloys, alloyed, martensitic steels, annealed cast iron. Another application area of «Kiborit» is structural ceramics, for example inserts for HPA to create higher pressures (in some cases up to 40 GPa), and conduct research on substance under pressure –insity, due to the X-ray diffraction of the «Kiborit» for synchrotron radiation. A new application area of the tool from «Kiborit» is the friction welding with mixing (FWM).

One of the main problems at the FWM of the high-temperature materials is the correct choice of the tool material. Usually there are refractory metals or ceramic materials - unalloyed tungsten, tungsten carbide, tungsten-rhenium alloy, cobalt-nickel alloys, as well as polycrystalline materials based on cubic boron nitride. The latter due to their unique mechanical characteristics are often the only materials capable of withstanding high loads and temperatures during welding.

The working tool for the FWM was made from «Kiborit-2» [1, 2] .. This material was chosen due to the best combination of hardness, fracture toughness, thermal conductivity and requirements for geometric dimensions of the tool. To obtain the workpieces, a high-pressure cell, where sintering of the powder mixture cBN and Al is carried out, was modified so that the subsequent machining of the detail is minimized.

Tool testing from «Kiborit-2» for FWM was carried out at The scientific and production company «IEWP» during the restoration of copper plates for cooling crystallizers of continuous castings and nickel coating on copper plates. A continuous coating of copper with a thickness of 4 mm, or of nickel - 3 mm was deposited on the copper plate by the friction welding deposition with mixing (FWDM). Thus, using the tool from «Kiborit-2», technological methods of welding copper and nickel on copper plates of large thickness by the FWDM method have been developed. An experimental technology of nickel coating deposition on copper plates of crystallizers for the steel continuous casting with the FWDM method was developed and tested.

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2. Новиков Н.В., Шульженко А.А., Беженар Н.П. и др. Киборит: получение, структура, свойства, применение // Сверхтвердые материалы.- 2001. №2.- С. 40 - 51.

HPHT REACTION SINTERING THE cBN – DIAMOND – SiCw–Al AND cBN–DIAMOND–Co–Al COMPOSITES

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The results of phase's formation in the reaction sintering cBN–diamond–SiCw–Al and cBN–diamond–Co–Al samples were considered. The composite materials of mentioned system are perspective for use ones for making structural parts (component of high pressure set, friction and rolling pairs, other) and cutting tools.

The micropowder KM 10/07 and ACM 5/3 (made in Bakul Institute for Superhard Materials, Ukraine); Silar® SC-9M (ACM, LLC; USA) SiC wicker; Al powder with 20/10 graininess, isolated from PAP – 2 powder GOST 5494 – 95 and Co micropowder was used as a starting materials for samples sintering too. The content of Al powder in all working mixtures was 10 % mass percent. The sintering experiments were carried out with "anvil with hole" type high pressure device, equipped with R6M5 steel die block (made in Bakul Institute for Superhard Materials, Ukraine). The samples were taken at a pressure 4,5–4,8 GPa and temperature 1400–1450 ^{o}C for 240 seconds.

Diffraction patterns of samples obtained by sintering from a charge with initial compositions 65 % KM10/7–20 % ACM5/3–5 % SiCw–10% Al20/10 and 62 % KM10/7–20 % ACM5/3–8 % Co–10 % Al 10/5 are presented in Fig. 1 and 2, accordingly.
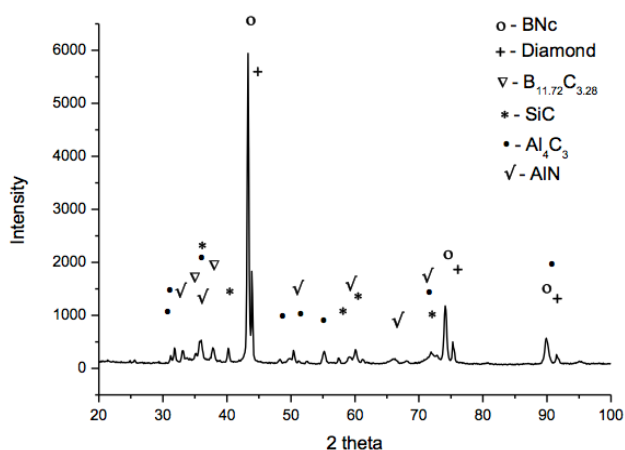
Fig. 1
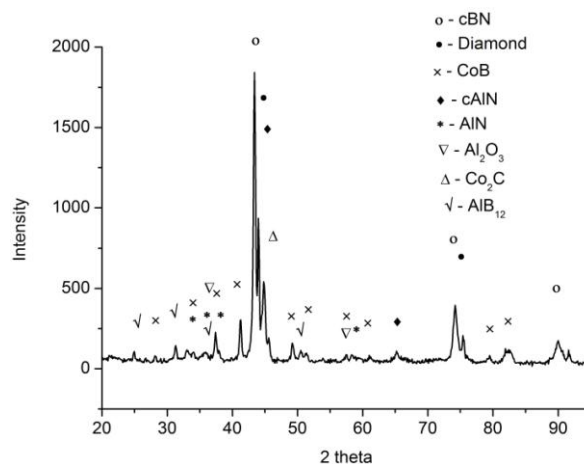
Fig. 2

The phase composition of the samples, shown on the diffraction patterns, shows that during their sintering, the reactive interaction of the initial components of the charge takes place. The formation of new phases, thanks to which a high level of physicomechanical characteristics of the samples is provided, is a result this interaction.

When the samples are sintered in the cBN-Diamond–SiCw–Al system (see Fig. 1), as a result of the reaction interaction of the initial components of the charge, boron carbide, aluminum nitride and aluminum carbide - new phases are formed. These phases are characterized by high hardness and wear resistance and their formation is a positive process.

Specific for samples obtained by sintering in the cNB-diamond-Co-Al system is the formation of cobalt compounds such as CoB (the result of the interaction of Co and cBN powders) and Co_2C (the result of the interaction of Co and diamond powders). It is characteristic that formation aluminum carbide in the considered system is not fixed.

COMPOSITE MATERIAL cBN-VC-Al.

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Constantly growing needs of the processing industry are driven by the search and development of cutting materials with increased wear resistance.According to ISO 1832: 2017 [1] cutting tools for high-speed machining corresponds to BLgroup consist ofcBN(40 - 65 vol.%) and binder in form of refractory compounds TiC, TiN, TiCN. Vanadium carbide, which according to it physical and mechanical properties is similar to the commercial binder-titanium carbide, was chosen for the development of a composite based on cBN.

Commercially available powders of cubic boron nitride cBN (Element Six) and vanadium carbide (Alfa Aesar) were chosenfor sintering of cBN:VC:Al (50:45:5 vol%). Sintering of samples were carried out in a high-pressure high-temperature toroid type apparatus TOR-30 in the temperature range of 1450 °C - 2450 °C,under 7.7 GPa for 45 s. The phase composition remains unchangedin the range of sintering temperatures 1450 °C - 1850 °C (Fig. 1).
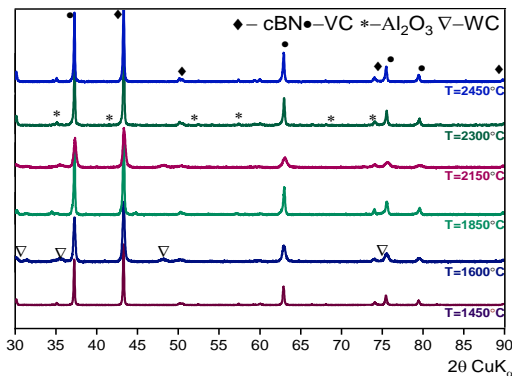
Fig. 1XRD patterns of cBN:VC:Alsamples, $T_{s.}$ *= 1450 °C – 2450 °C, P = 7,7 GPa, τ = 45 s.*

The interaction between components, namely, the oxidation of aluminum, begins at sintering temperatures ≤ 2150 °C, as evidenced by the appearance of peaks of Al_2O_3phaseon XRDpatterns. Microhardness of composites $T_{s.}$ = 1600 °C equal to 31 GPa

(Fig. 2). Further increase of sintering temperature from 1600 °C to 2150 °C causes annealing of structural defects, which leads to a decrease in microhardness to 25 GPa. Fracture toughness of samples particularly not affected by sintering temperature and stay around 5.2 - 5.4 MPa·m$^{1/2}$.
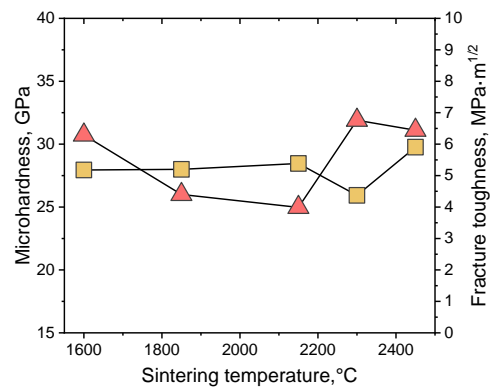
*Fig. 2Influence of sintering temperature on microhardness and*fracture toughness *of samples in systemcBN:VC:Al*

Performance testing of cBN:VC:Al (50:45:5 vol.%) samples in machining of stainless steel AISI 316L showed that at cutting speed v_c = 300 m/min, the average flank wear of the samples does not exceed V_B = 300 μm, the highest wear resistance found in sample $T_{s.}$ = 2300 °C - V_B = 88 μm.

Taking into account the physical and mechanical properties, it was found that the optimum temperature interval forHPHT sintering under pressure of 7.7 GPa is 2300 °C - 2450 °C. Microhardness of samples is close to commercial CBN100 (E6 England).

[1]"ISO 1832:2017 Indexable inserts for cutting tools -- Designation," vol. 2017, 2017.

LOW-TEMPERATURE SYNTHESIS OF HIGH-DENSE BORON CARBIDE BASED CERAMICS

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Boron carbide is an important high-strength non-metallic material with high melting point, chemical resistance, wear resistance and low density. The combination of these properties causes the use of boron carbide in many aplication: military industry, mechanical engineering, electronics, energy, and others. The high mechanical characteristics of the carbide are due to the strong covalent nature of its chemical bond. However, the nature of the chemical bond is a source of complexity that arises during the consolidation of ceramics based on boron carbide. For the production of ceramics from boron carbide, various methods of sintering are used: hot pressing, spark plasma sintering, traditional sintering, infiltration, etc. Recently, the method of infiltration of boron carbide by silicon melt is becoming more and more popular, since this method does not require high temperatures, it allows to receive high-density products of complex form and is energy-efficient. However, residual silicon, which is formed in the process of infiltration, significantly reduces the mechanical characteristics of the resulting ceramics. In order to reduce the content of residual silicon, it is proposed to apply a zone melting method that allows melting only one component (silicon), which will reduce its content in the "free" form. Moreover, the presence of a temperature gradient field should provide for the crystallization of boron carbide through a silicon melt, allowing ceramics with almost monolithic structure to be obtained.

Thus, the purpose of this work was to establish the possibility of obtaining high-density boron carbide based ceramics, by zone melting of the fusible component (silicon) using porous samples. Powder mixture of boron carbide B_4C and silicon (1-10 vol%) were used as starting components. In order to determine the influence of the sample velocity in the field of the temperature gradient samples were obtained with the speed of the inductor moving 0.5-2 mm/min. During the work microstructure, phase composition and mechanical characteristics of boron carbide based ceramics were controlled.

Studies of the microstructure of specimens with different silicon content showed that 10 vol.% of silicon is sufficient to form a zone of its melt and recrystallize boron carbide through the melt. It is shown that depending on the velocity of the field of the temperature gradient, the microstructure of the resulting ceramics is changed. Thus, at a minimum speed (0.5 mm/min), almost monolithic boron carbide is formed. With increasing speed up to 1.5 mm/min there is a grinding of boron carbide grains in comparison with the minimum speed. That is, the inhibition of the growth of grains of boron carbide and the formation of monolith. Moreover, there are inclusions of silicon carbide that have an elongated shape. It was also found that the secondary silicon carbide formed has a hexagonal structure, which determines the elongated shape of the grains. The residual silicon content for the samples obtained was less than 2 wt.%. Depending on the place where the resulting ceramics were embedded (monolithic boron carbide or inclusion of silicon carbide or residual silicon), the hardness varied from 33-35 GPa (boron carbide), 19-21 GPa (silicon carbide) and 8-11 GPa (silicon).

As a result of the research, it is shown the possibility of obtaining high-density boron carbide based ceramics by its recrystallization in the field of a temperature gradient through a silicon melt with the remaining silicon content of less than 2 wt.% is shown.

INFLUENCE OF CARBON FIBERS ADDITION ON THE MECHANICAL PROPERTIES OF BORON CARBIDE BASED CERAMICS OBTAINED BY INFILTRATION METHOD

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Boron carbide is a representative of refractory compounds and related to superhard materials. Due to the combination of such properties as: low density, high hardness, high melting point, unique heat and electrical conductivity, materials based on boron carbide have found their application as cutting tools; armor protection, wear-resistant materials; materials for the absorption of electrons, etc. At the same time, the refractory nature of boron carbide significantly complicates the sintering process of ceramics on its basis, and hence obtaining massive products. For the production of ceramics based on boron carbide, the hot pressing method (HP), spark-plasma sintering (SPS), hot isostatic pressing (HIP) and conventional sintering (CS) without pressure are used. However, HP, SPS and HIP methods significantly limit the dimensions and shapes of products, and CS without pressure requires high temperatures (over 2300 ° C) and long exposures. Another method for producing of high-density ceramics based on boron carbide is the infiltration of the porous billet with a silicon melt. The main disadvantages of ceramics obtained by infiltration are a large amount (more than 10% by weight) of residual silicon, which significantly reduces the mechanical properties of ceramics based on boron carbide. It is known that the most effective method of increasing mechanical characteristics is reinforcement. That is why the influence of the amount of reinforcing carbon fibers on the structure, phase composition and mechanical characteristics of ceramics based on boron carbide is established in the work. The choice of carbon fibers as a reinforcing component is explained by their high strength and module of elasticity, 2 ... 3.5 GPa and 220 ... 700 GPa, respectively. Moreover, as a result of the reaction between silicon and carbon fibers, the formation of secondary silicon carbide was assumed, which also has high mechanical characteristics. As starting materials were used: boron carbide powder (B_4C, 95%, JSC Zaporozhabraziv), silicon powder (Si, 99.0%, Chim. Reactiv Co. Ltd., Ukraine) and carbon fibers (HTA 40, Toho Tenax Europe GmbH, Deutschland) A pre-formed mixture of B_4C powder and various amounts of carbon fibers (0, 5, 10, 15, 20 wt.%) was impregnated with silicon melt. Three-point bending mechanical testing revealed that increase in the concentration of carbon fibers to 10% by weight leads to an increase in the strength of the ceramics from 350 MPa to 510 MPa. A further increase in fiber content leads to strength reduction up to the strength of pure boron carbide. This behavior can be explained by the formation of coils (agglomerates) of fibers during mixture preparation. As a result the formation of aggregates (up to 100 mμ) of silicon carbide and carbon during the infiltration process, which was found during microstructure studies. However, it should be noted that ceramics with an initial content of carbon fibers of 10 wt.% and 20 wt.% showed high values of the modules of elasticity by 10 % and 15 %, respectively. It was found that the amount of fibers determines the phase composition of the resulting ceramic. Thus, it has been shown that the addition of fibers of more than 10 wt% causes the formation of a phase of hexagonal silicon carbide, which can serve to increase the modulus of elasticity of ceramics.

PECULIARITIES OF INTERPHASE INTERACTION OF EPOXY OLIGOMERS WITH METALLIC FILLERS

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The formation of the structure of instrumental composite materials on polymer binders is not limited to solidifying the oligomer and forming a three-dimensional molecular network. Obvious criteria, as well as physical and mechanical characteristics of the bundle, only indirectly characterize the functionality of the material. More promising is the study of the influence of technological parameters on the amount of free volume of the polymer. This structural parameter allows us to link the dynamic characteristics of the polymer network, the composition and the technological history of the bundle into a single complex. A necessary intermediate step in the analysis of the free volume of polymers in instrumental composites is the study of the orderliness of the polymer structure and the interphase interaction of oligomers with the filler surface, in particular diamond, and also metals.

In the process of structural and functional optimization of the developed instrumental composites, the interfacial interaction of the components of oligomeric binders with the surface of copper powders and intermetallide Ni_3Al was studied. In particular, the change in vibration frequencies of reactive bonds of adsorbed oligomer molecules indicates their segregation by reactivity and, accordingly, the rate of entry into the polymerization reaction, as well as by the energies of adsorption interaction with the active centers of the surface of particles of metal powders and intermetallides. As a result of the analysis of the thermal desorption spectra of fragments of oligomer molecules from the surface of the filler particles, the existence of two types of adsorbed molecules (for metals) and three (for intermetallide Ni_3Al), differing in the interaction energies with a solid surface

The degree of polymer ordering in the system under investigation is determined by two main aspects. First, there is a genetic link between the structure of polymer layers structured near the surface of the filler particles and the structural features of the original polymer. Secondly, the fragments of the polymer network, which differ significantly in conformational possibilities from the initial molecules of the oligomer, also change the spatial position due to interaction with the surface of the solid. The presence of a preferential orientation of the sections of polymer chains in the system studied is confirmed by a change in the intensity of absorption bands of IR spectra at a frequency of 810–830 cm^{-1}. As it turned out, when the system is cured, the orderliness at the level of functional groups is partially destroyed, but at the level of individual segments in the composition of the polymer network, the polymer structure remains regular. This is confirmed by data obtained by X-ray small-angle scattering.

The data obtained make it possible to improve the understanding of the processes of structure formation in the filled polymer systems, which is necessary for developing new, more effective criteria for optimizing the technological regimes for manufacturing diamond-containing materials on polymer bonds.

HYBRID OLIGOMERS CONTAINING METAL IONS

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Modification of epoxy oligomers was carried out in order to obtain two-level polymer systems capable of being in different structural states, and thus prone to spontaneous reversible structural rearrangements in accordance with the conditions arising in the zone of dynamic contact. The original oligomers were reacted with components containing several functional groups that formed chemical coordination bonds with metal ions having unfilled inner electron shells.

As modifying agents, copper and nickel complexes with aminopropionic acid containing several potentially complex-forming donor groups ($-NH_2$, $-CO-$) were chosen as starting epoxy oligomers – ED-24 and higher-molecular ED-20. The use of these initial resins individually or in various proportions gives "structural elements" of a polymer network of various lengths. Of these, it is possible to form polymer structures with different alternations of the epoxy fragments themselves and the coordination bonds introduced during the modification process.

Aminocomplex metal derivatives were introduced into the composition of epoxy oligomers in an amount of 5–20 mol. %. Modified products were examined by gel permeation chromatography. Chromatograms fix the overall increase in molecular weight of the modified oligomers. The kinetics of the interaction of modified compounds with epoxy oligomers was evaluated by increasing the dynamic viscosity during the reaction. The criterion for completion of the reaction was the termination of an increase in the viscosity of the system with an increase in the residence time under the reaction conditions. It was found that the number of products with increased molecular weight increases without changing the structure of the metal complex fragment. In parallel, some elongation of the oligomer chains occurs.

The curing characteristics of the oligomers obtained are largely determined by the content in their structure of a large number of metal complex fragments. The most common hardeners, in particular anhydrides, as well as primary and secondary amines, reacting with epoxy groups, destroy metal complex fragments already at an early stage of curing. This disrupts the genetic link between the structure of the initial oligomer and the resulting polymer network.

The mechanism of this phenomenon seems to be in the competition between the amino groups of the modified oligomer and the functional groups of the hardeners of these types for the possibility of coordination with the central metal ion. 2-ethyl, 4-methylimidazole proved to be an effective hardener, allowing to preserve the coordination environment of metal ions.

Analysis of the structure of polymers obtained by curing hybrid oligomers containing metal ions showed the presence of two types of fragments. One of them is the areas with the structure of tetraamine complexes. The second is fragments with a chelate structure. Internal stresses caused by the formation of a three-dimensional spatial grid of epoxy polymer significantly reduce the potential barrier of mutual transition of the two structural states mentioned.

This creates the prerequisites for the formation of abrasive and antifriction composites, which are two-level systems capable of reversibly changing the structure and properties under variable external conditions.

DYNAMICS OF WC+25 wt. % Co POWDER MIXTURE DENSIFICATION DURING IMPACT SINTERING

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The densification of a fine-grained tungsten-carbide-based cermet with a 25wt% cobalt binder during the impact sintering at temperatures of 1150, 1200, 1250 and 1300 °C in vacuum with an initial impact velocity of 5.8 and 6.2 m/s provided the initial solid-phase state of the binder was studied. The choice of temperature was made taking into account the liquid phase appearance during the sintering of WC–Co cemented carbides in the temperature range from 1300 to 1320 °C.

Based on the obtained experimental data and the calculated characteristics of the elastic properties of samples and the impact machine, the modeling of the compaction dynamics using a third-order dynamic system [Ref.] was carried out by trial and error procedure, and the shear viscosity of the cermet matrix determining the energy dissipation in the system and the irreversibility of the material densification were obtained.

The solutions of dynamic system give the dependences of the linear compression, velocity, and acceleration of the system upon time.
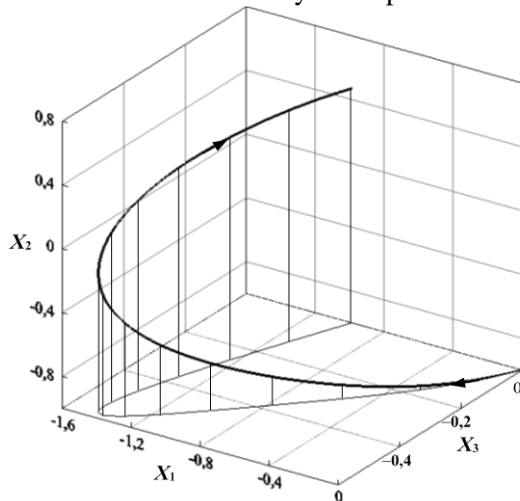
The figure shows the phase trajectory of dynamic system movement in three-dimensional space $X_1X_2X_3$ (where X_1, X_2, and X_3 are the linear dimensionless compression, velocity, and acceleration of the system respectively) for impact sintering the cermet sample at the temperature of 1150 °C, initial impact velocity of 5.8 m/s, and the reduced mass of machine impact parts of 367.4 kg.

The phase trajectory of the system from the beginning of the densification to the elastic rebound of the impact parts of the machine showed that not all the kinetic energy of the impact transforms into the work of irreversible deformation of the porous cermet. The unused portion of the kinetic energy is dissipated in the environment that is consistent with a phenomenon of the real (imperfect, not pure elastic) impact.

The data above enable to determine force generating during the impact action versus time as well as the time dependences of dimensions and relative density of samples. The results of the mean square strains at a rate and stresses determination in cermet samples during their impact densification show that the matrix porous body is most intensively deformed at the initial stage until the peak force value is reached.

The obtained data also includes the duration of the impact loading which is equal approximately 3 ms as well as the work of densification and the mechanothermal effect as a result of energy dissipation which provide a substantial increase in the temperature of porous cermet samples. Since the initial samples temperature is close to the temperature of eutectic formation, and the initial samples porosity is low, the mechanothermal effect can cause the squeezing of liquid phase out of the sample into a porous graphite shell that protects the samples from sticking to the metal press form.

The estimated activation energy of porous cermet matrix material viscous flow is 1.1 eV or 103 kJ/mol.

According to the results of calculations, the samples temperature increase caused by mechanothermal effect is significant and reaches the values from 33 K up to 243 K. Such a result enables to assume that the liquid eutectics may appear at the final stage of impact sintering in case of tungsten carbide dissolution in cobalt occurs during a short (millisecond) sintering time.

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Kovalchenko M. S., Laptev A. V. Dynamics of WC–Co Hard Alloy Compaction with Hot Pulsed Pressing // Powder Metall. Met. Ceram. – 2004. – Vol. 43, Nos. 3-4. – P. 117–126.\

DIAMOND POLYCRYSTALLINE COMPOSITE MATERIALS OBTAINED BY HPHT SINTERING WITH THE USE OF n-LAYER GRAPHENS

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Among the variety of nanostructural elements chosen as modifying additives, a promising direction is the use of graphenes possessing a unique complex of physical properties. In the V.N. Bakul ISM NAS of Ukraine, active research is being carried out to obtain new diamond composite polycrystalline materials of various functional design, characterized by increased wear resistance, electrical or thermal conductivity activated by sintering diamond powders with the addition of n-layer graphenes[1–4].

In experiments, micropowders of synthetic and natural diamond and n-layer graphene powders of two types were used as starting materials: in graphene Gn (4), the particles consisted of nanoplates presented as a stack from less than four layers and graphene N 002-PDR presented as stack from less than three layers of graphene.

A new wear-resistant superhard diamond composite material with a strength of 35% higher and wear resistance at the turning of the IX drilling category sandstones in 4–7 times higher than in polycrystals obtained without the addition of graphene [4]. was produced by activated sintering at the HPNT conditions of diamond micropowders with the addition of n-layer graphenes in an amount of 0.05–0.20% by weight.

A significant increase in the physicomechanical characteristics is achieved due to the formation of a more dense and homogeneous structure with the participation of graphene due to the reduction of friction and wedging between the diamond particles during the cold compaction of the diamond powder at high pressure.

It has also been established that with an increase in the content of graphene in a diamond polycrystalline compact, the resistivity decreases sharply (almost fourfold). With the same content of n-layer graphene in the polycrystalline composite, its resistivity depends on the size of the diamond grains, and when using graphene with a smaller number of layers, the resistivity increases significantly (by two orders of magnitude) [3]. The results of the study of the temperature dependence on the electrical resistivity showed that with increasing temperature the resistance of the samples decreases, which is typical for the semiconductor type of conductivity.

A method has been developed that includes a two-stage dry blending regime for diamond powders and n-layer graphenes, which differ sharply in density and particle size [4], which made it possible to provide a dense and homogeneous structure of the composite, and ultimately to increase the thermal conductivity of the composite by matching the intergrain contacts and phonon fluxes.

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HIGH TEMPERATURE MATERIALS OF SYSTEM Nb-Si-B

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Scientific and technological progress requires the creation of new materials capable of operating under conditions of high temperatures, velocities, loads and corrosive environments, as well as possessing high physico-chemical and mechanical properties, due to which such materials are capable of operation under extreme conditions. To date, such materials are widely used in the aviation, missile, nuclear industry [1].

The production of reinforced ceramic materials by mixing the matrix phase and fiber powders followed by sintering, hot pressing, isostatic pressing does not allow preserving the integrity and uniform distribution of fibers in the volume of the matrix phase.

The methods of crystallization from melts of eutectic alloys make it possible to obtain a regular arrangement of fibers and formation of coherent and semicoherent boundaries of the distribution between the matrix phase and fibers, which is the main condition for increasing the thermal stability of the structure and improving the physico-mechanical properties of the material [2].

The main condition for the formation of reinforced ceramic materials by crystallization from melts is the eutectic character of the state diagram.

Using the electron-beam melting method, alloys of the Nb-Si-B system were obtained. The scanning electron microscopy, microspectral, quantitative metallographic and X-ray phase analysis were used for researching the microstructure, the shape and dimensions of the phase components, the chemical and phase composition of the alloys.

The microhardness and fracture toughness of the obtained alloys are studied by the method of durometric analysis. The microstructure of the eutectic alloy of the Nb-Si-B system is shown in Fig. 1.

For an alloy with such a composition, crystallization does not occur in the temperature range, but at the temperature of formation of the eutectic (1850 °C), consisting of small crystals of both components.

It was established the matrix is a solid solution of niobium, and the inclusion is the phases of Nb_5Si_2B and Nb_5Si_3 by microspectral and X-ray phase analysis.
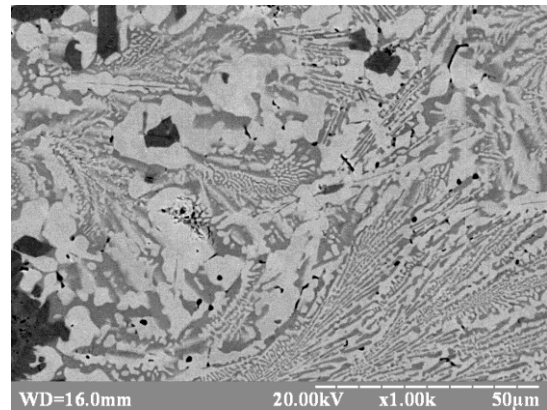
Fig. 1. Microstructure of the eutectic alloy Nb-13Si-7B

As is known, microhardness is influenced by such factors as atomic-crystalline structure, chemical composition, microstructure, morphology of phase constituents, porosity. It is established that the interhalic microhardness of the eutectic alloy of the Nb-Si-B system is 12 GPa, which can be explained by a more dispersed and homogeneous structure. And the fracture toughness is 11.2 $MPa*m^{1/2}$, which can be explained by the plasticity of the matrix phase from the solid solution of niobium, which is a barrier to the formation of structural defects.

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PREPARATION OF ZIRCONIUM NITRIDE POWDER BY THE CARBOTHERMAL SYNTHESIS METHOD

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Zirconium nitride, due to the combination of the ionic, covalent, and metallic types of chemical bond, exhibits high hardness, very high melting point, good thermal and electric conductivity. One of the methods of preparation of zirconium nitride powders and fibers is the method of carbothermal reduction-nitriding. This method makes it possible to obtain nanodisperse powders with the use of reaction mixtures prepared by the solution technology.

The objective of the present work is to investigate the process of carbothermal reduction-nitriding of mixtures prepared by the solution method with the use of different oxygen-containing zirconium compounds and sucrose.

In the work, as initial substances, commercial powders of zirconium oxide ZrO_2, zirconyl nitrate $ZrO(NO_3)_2 \cdot 2H_2O$, zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$ and sucrose $C_{12}H_{22}O_{11}$ were used.

Mixtures were prepared by the solution method with the use of distilled water as a solvent. ZrO_2 suspension, $ZrO(NO_3)_2 \cdot 2H_2O$ and $ZrOCl_2 \cdot 8H_2O$ solutions were mixed with sucrose solutions. The obtained mixtures were dried in air at 100 °C and subjected to pyrolysis at a temperature of 600 °C in a nitrogen flow for 2 h. The pyrolyzed mixtures were subjected to mechanoactivation in a "Pulverizette" ball mill in the regime 400 rpm for 1 h and nitrided in a SUOL-type furnace in a nitrogen flow at temperatures of 1200 and 1300 °C with holding for 3 h.

The contents of nitrogen and carbon in powders obtained from mixtures of different Zr-containing compounds and sucrose at nitriding temperatures ($T_{nit.}$) of 1200 и 1300 °C with holding for 3 h are presented in the table. According to the data of the chemical analysis of the nitriding products, the mixtures containing ZrO_2 and sucrose showed the highest degree of nitriding, whereas the mixtures containing zirconium oxychloride and sucrose revealed the lowest degree of nitriding. All synthesized powders contained residual nonreacted carbon.

According to the data of X-ray phase analysis, in all nitriding products, along with ZrN, the ZrO_2 phase was present (Figs. 1 and 2).

Initial compounds	$T_{nit.}$, °C	Content, mass %	
		N	C
$ZrO_2+C_{12}H_{22}O_{11}$	1200	6,9	2.7
	1300	10,5	1.1
$ZrO(NO_3)_2 \cdot 2H_2O+C_{12}H_{22}O_{11}$	1200	6.1	2.9
	1300	8.5	2.6
$ZrOCl_2 \cdot 8H_2O+C_{12}H_{22}O_{11}$	1200	4.2	3.2
	1300	6.7	2.8
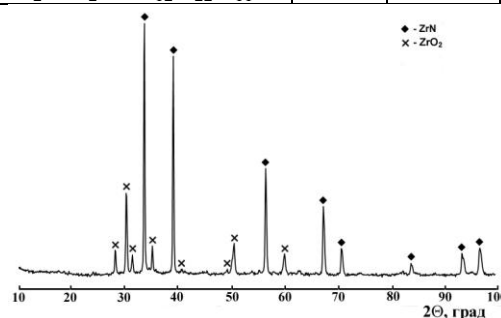
Fig. 1. X-ray diffraction pattern of the product of nitriding of the ZrO_2–$C_{12}H_{22}O_{11}$ mixture at a temperature of 1300 °C for 3 h
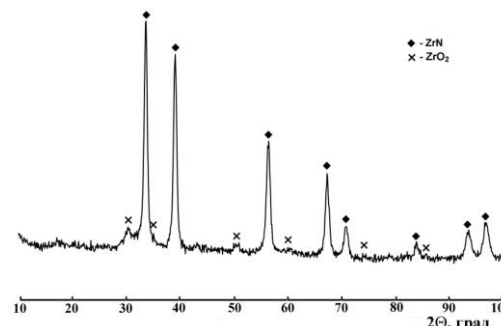
Рис. 2. X-ray diffraction pattern of the product of nitriding of the $ZrO(NO_3)_2 \times 2H_2O$–$C_{12}H_{22}O_{11}$ mixture at a temperature of 1300 °C for 3 h

The results of the investigation showed that the highest nitrogen content (10.5 mass %) was obtained in powders synthesized from the ZrO_2–$C_{12}H_{22}O_{11}$ mixture at 1300 °C with holding for 3 h. The presence of ZrO_2 and residual carbon in the nitriding products is explained by the incomplete reduction of the initial zirconium compounds and indicates the necessity of using a more active hydrogen-containing nitriding atmosphere.

ALLOYS OF THE SYSTEM Cr_3C_2-ZrB_2

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Many years of research show that ceramic materials are the strongest structural materials, but at the same time they are relatively unreliable, since they are not destroyed by the gradual loading, as is the case with metals and alloys, but instantaneously at loads above the critical one, which is determined by the formula [1, 2]:

$$\sigma = \frac{K_{1C}}{\alpha\sqrt{L}} \ , \qquad (1)$$

where σ – is the critical stress of destruction, K_{1C} - is the fracture toughness, L – is the defect size, crack, α – is the geometric constant.

As can be seen from formula (1), the critical decay voltage is determined by two values: the size of the defect L L and the degree of viscosity of the destruction of K_{1C}, for which the indentation method is often used by the formula [3, 4]:

$$K_{1C} = \frac{0,072 \cdot H \cdot a^{0,5}}{\left(\frac{c}{a} - 1\right)^{0,34}} \qquad (2)$$

where H – is microhardness, a – is half the diagonal of the indenter, c – is the distance from the center of the indentress to the end of the crack.

Thus, in order to increase the magnitude of the critical load, it is necessary to control the structure of the material in accordance with the requirements of the maximum value K_{1C}, the actual factor of inhibition of the crack.

Braking of a crack in metal alloys is due to the "shielding" of its peak by stress and interaction with the elements of heterogeneity of the structure. In ceramic materials, the most effective shielding of the crack occurs when the material contains fibers that have virtually theoretical strength.

Quasibinar alloys of eutectic systems are promising structural high-temperature materials.

In this paper, quasibinary alloys of the system Cr_3C_2-ZrB_2. ZrB_2 were investigated. Samples from a mixture of powders of various composition were melting in the electron beam unit «ELA-6». ". The melting temperature was measured using a pyrometer with an accuracy of ± 50 °C. The fusion diagram is eutectic. The content of zirconium diboride in the euthectic system of the Cr_3C_2-ZrB_2 system is 15± 2,0 mol. %, and the melting point of the eutectic alloy is - 1650 °C. The structures of the alloys are shown in Figure 1. In the eutectic alloy, zirconium diboride crystallizes in the form of rods (light phase in Figure 1).

| a | б |
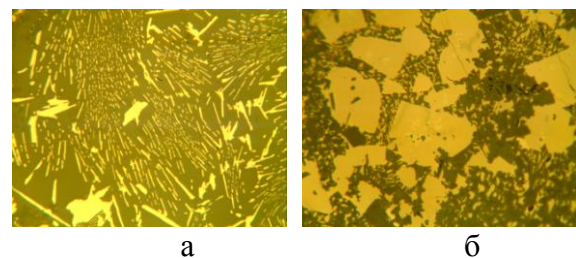
Fig. 1. - Microstructure of alloys of the system Cr_3C_2-ZrB_2: a – eutectic alloy (Cr_3C_2-15 mol% ZrB_2) , б – zeutectic alloy (Cr_3C_2-50 mol% ZrB_2)

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ON CONTACT MELTING AT THE PERITIC CRYSTALLIZATION OF THE STEEL

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At peritectic crystallization of alloys with both packed low-temperature and loosely packed high-temperature phases, shrinkage shells (so-called peritectic cracks) are often formed. They are oxidized, and not brewed during hot rolling and can cause destruction of the cast slab. In order to develop technical recommendations for the removal of cracks, a study of the microscopic kinetics of boundary

location (in Fig. 1, b-d are indicated by the arrows P_{kn}). Subsequent saturation of this liquid with iron causes its transformation into austenite, the formation of a new δ / γ boundary, and the process is repeated Through the channels with the interdendritic liquid $P_{мд}$, the shrinkage shells are replenished and healed.
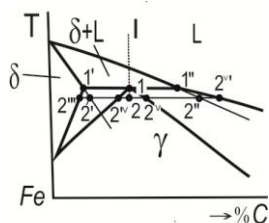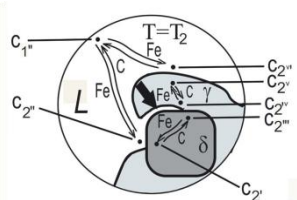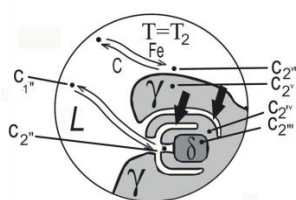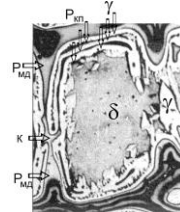
а   б   в   г

peritectic transformation into steel was made by means of the thermodynamics of irreversible processes (transfer version). The equilibrium local concentrations at the interphase boundaries was determined from the phase diagram of Fe-C (Fig. 1, a), then concentration gradients were established and local diffusion fluxes were determined in each of the three interacting phases (Fig. 1, b)

It is established, in particular, that after the nucleation and growth of the low-temperature γ phase on the surface of the maternal δ phase during reaction L + δ → γ, the boundary zone is supersaturated with carbon due to the diffusion of C atoms to the common boundary δ / γ. It causes the contact melting to form liquid-phase channels on the **Conclusion.** Liquid-phase channels are

formed as a result of the rather slow diffusion of C atoms through solid phases. Therefore, in order to successfully control peritectic cracks for each steel grade, it is necessary to determine experimentally the maximum permissible cooling rate in the crystallization temperature range.

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EFFECT OF THE RELATION OF THE SIZE PARTITIONS OF MIXTURE COMPONENTS ON THE ELECTRIC CONDUCTIVITY OF HYPEROGENEOUS MATERIAL Cu-W

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Composite materials based on copper powder, which contains a component of a heavy refractory phase in the mixture, are of practical interest for increasing the cumulative effect.

Material based on copper with 50 % wt. tungsten has a strength of $\sigma_p = 120$ kg/mm^2, a high specific gravity of 19.3 g/cm^3 and a relative elongation of 10 %, and increases the set of service properties at the time of breakdown.

The combination of such strength and plasticity indicators of copper and tungsten particles in the cumulative jet make it possible to create high indices during the operation of cumulative charges [1-3].

The aim of this work is to determine the effect of the ratio of the matrix – inclusion particle size on electrical conductivity and the physic-mechanical properties of the compacting material Cu – 50 % (wt.) W.

Powdered copper powder (Cu) of 40 and 100 μm particles and tungsten with an average particle size of 10 μm and 100 μm were used as the starting powders.

Samples were made by precision double-sided pressing to the stop (GOST 29012-91) with a pressing force of 63 T on a P-483 press.

The density of samples measuring 4.36 x 6.3 x 43.6 mm^3 was determined by the calculation method in accordance with GOST 18898-89.

The electrical conductivity and physic-mechanical properties of a cold-pressed heterogeneous material based on copper and inclusions (W), depending on the ratio of particle sizes of the matrix-inclusion component, are presented in the table.

The patterns of formation of the material structure are determined depending on the ratio of the particle sizes R (Cu) / R (W).

The electrical conductivity of the material was measured at room temperature using a DC bridge P30009, the measurement error was not more than 5 %.

The nature of the destruction of the heterogeneous material Cu – 50 % (wt.) W depending on the ratio of the particle size of the matrix – inclusion was investigated.

Table. Dependence of physical and mechanical properties of Cu-50% (w) W material on the ratio of the particle sizes of the components of the R (Cu) / R (W) mixture.

Particle size Cu, μm	R(Cu)/R(W)	Elastic modulus E, GPa	Strength on the bend, σ, MPa	Specific electrical resistance, ρ, Om· mm^2
40	-	98	49,5	0,0650
100	-	84	45	0,0489
40	4	94	40,2	1,692
40	0,4	94	44,4	0,0873

Investigations of cold-pressed materials Cu – 50 % (wt.) W showed that the ratio of the particle sizes of the matrix-inclusion R (Cu) / R (W) has a variation of up to 20 % on the physic-mechanical properties of the heterogeneous material.

It has been established that the value of the specific electrosupport of the pressed heterogeneous material based on the plastic matrix and tungsten inclusions can be corrected by varying the ratio of the particle size R(Cu) / R(W).

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INFLUENCE OF THE OUTPUT hBN ON THE CHARACTERISTICS OF THE SYNTHESISED cBN POWDERS

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Boron cubic nitride (cBN) in the form of powder of a wide range of grains is obtained by phase transformation at high pressure and high temperature from hexagonal boron nitride (hBN). Characteristics of hBN, which is used as one of the main components of the reaction mixture for the synthesis of cBN, along with the parameters of the synthesis process and the composition of the initiators of the hBN→cBN transformation signi-ficantly affect the degree of conversion of hBN→cBN and the graininess of the synthesis product.

The effect of the grain composition of both the initial and additionally mechanically activated hBN on the characteristics of the synthesized cBN powders was investigated in this paper.

The analysis of the grain composition of the output hBN in the delivery state showed that it consists of dense aggregates of grain sizes from several to about 80 μm, formed by separate, shallow-dispersed grains, close to each other by theis forms.

Experiments on its synthesis were carried out to evaluate the effect of the size of the grain aggre-gates on the crystallization process of cBN using one of the components of the reaction mixture of grains-agarates of hBN grains 80/20 μm and less than 5 μm. It is shown (Fig. 1) that when using hBN more coarse-grained powders, cBN grains are obtained in smaller quantities, but larger in size.

a	*b*
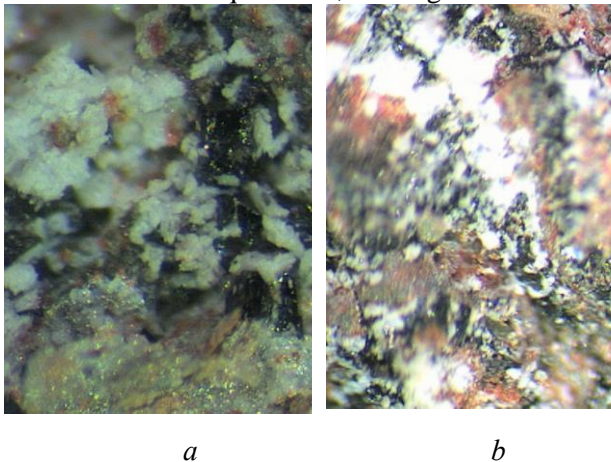
Fig. 1. Sinters with cBN grains obtained from hBN grains-aggregates of 80/20 μm graininess (*a*) and less than 5 μm graininess (*b*)

The results of the study of the effectiveness of using cBN in the synthesis of mechanically dispersed (activated) hBN grains, which increases the degree of the conversion hBN→cBN and increases the content of fine grains in the synthesis product are presented in Fig. 2.
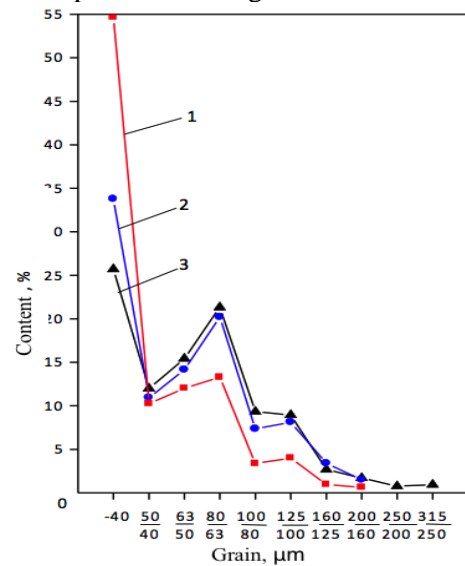
Fig. 2. The grain composition of cBN powders obtained with the use of dispersed hBN (1), with addition in the reaction mixture of dispersed hBN in an amount of 10 wt. % (2) and without the use of dispersed hBN (3)

The mechanical dispersion of the hBN powder was carried out in a planetary mill designed at V. Bakul ISM NASU.

Analysis of the grain composition of hBN powder after dispersion for 60 sec showed that it, as well as before the dispersion, consists of grain aggregates formed by fine dispersed mono grains the maximum size of which decreased to 50 μm, and the specific surface area increased from 0,787 to 1,025 m^2/cm^3.

As a result of the mechanical dispersion of hBN, its activity in the synthesis of cBN was significantly increased. Thus, the number of crystallization centers increased, resulting in increased content in the target product of cBN fine dispersed grains formed during the synthesis (see Figure 2).

INFLUENCE OF THE ENVIRONMENT ON THE PROCESSES OF AGGLOMERATION THICK-FILM CONDUCTIVE COMPOSITE MATERIALS ON THE BASIS OF REFRACTORY COMPOUNDS.

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The process of production of film resistive materials consists of the preparation of powder compositions in the form of pastes followed by their application by screen printing on a dielectric substrate. The final stage of the formation of physical and mechanical properties is thermal treatment in the temperature range 650-1000 °C. Functional particles of resistive pastes (RP) - powders of refractory compounds - during the sintering process must retain a solid state and mass contact, i.e. have a melting point of more than 900 °C.

The electrical conductivity of metal-ceramic films is determined by their structure and phase composition and assumes the presence of metallic, as well as activation types of conductivity (called tunneling and hopping-trapping) in nonmetallic interlayers between the particles of the conducting phase [1].

Therefore, the study of the reactions between the components of resistive compositions in the process of heat treatment in oxidizing (air) and reducing (CO) environments has an important scientific and applied significance. Heat treatment of pastes was carried out in an electric furnace type PEC-8M and in a reducing environment of a gas furnace type EK-21.

Resistive conductive pastes are a mixture of powders of a conductive material and a glass binding agent dispersed in an organic binder. As a result of the interaction of the metal component with the constant binder (glass), oxidation-reduction reactions occur at the interface of the two phases with the formation of new structural elements, depending on the atmosphere of the furnace, which affects the mechanism of electrical conductivity in the films, changing their resistance and the temperature coefficient of electrical resistivity.

It should be noted that incomplete removal of the temporary binder (organic binder) during sintering leads to the release of carbon forming carbides on the metal surface and to an increase in contact resistance. During the reaction with the glass phase, gases are released and the surface of the film is broken. In addition, the interaction between the glass phase of the substrate and the glass powder during melting is of great importance, the mutual solubility of which ensures the adhesion of the conductor to the substrate [2].

In resistive pastes, there are significantly more components than in dielectric and conductive, and therefore more opportunities for complex reactions during sintering. The carbidization of organic binders during sintering has the same effect as in conductors. The reactions of the glass phase of the substrate and the glass powder are more difficult because of the larger content of the glass and its more complex composition. When sintering resistive compositions, the reaction rate depends more on temperature than in conductive pastes. Therefore, for a good reproducibility of the results, it is necessary to strictly observe the sintering regimes and the atmosphere of the furnace.

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SPECIAL FEATURES OF THE STRUCTURE OF THE SINTERED MULTICOMPONENT COMPOSITE OF THE Ti-B$_4$C-Fe-Ni SYSTEM OBTAINED BY THE HIGH-TEMPERATURE SYNTHESIS METHOD

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To create high-strength composites, titanium powders with carbon or high-strength carbides are widely used in combination with an iron, steel or other plastic metal matrix. One of the effective technologies for high-temperature synthesis of materials based on titanium is the use as a raw material of powders of boron carbide B$_4$C, used instead of carbon powder. Such a replacement allows the creation of metal matrix composites reinforced with a high-strength carcass in which titanium carbide is enhanced by high-strength titanium boride.

The purpose of this study is to identify the most promising areas in the development of composite materials based on high-strength carbides and titanium borides eutectic composition embedded in a ductile metal matrix based on transition metals, establishing the basic patterns of structure formation, phase composition of the obtained composites of the Ti-B$_4$C-Fe-Ni system .

The structure of the composite is a porous conglomerate, 80% consisting of a refractory carbide carcass and titanium diboride embedded in a ductile iron-nickel matrix (Fig. a, b). Particles of the solid phase are located chaotically. The rupture is brittle, the fracture occurs by cleaving at incoherent interfaces between the grains of the synthesized phases. Crushing of carbide and boride grains is not observed, the carbide and titanium diboride grains are extracted from the plastic iron-nickel matrix. This indicates a low adhesion strength at the interface between the high-hard phase and the plastic matrix. Solid particles of carbides and borides have a characteristic crystalline facet, which indicates the ordered crystal structure of individual particles.

a)

C	13,35	35,6
O	4,83	9,67
Ti	81,82	54,73

b)
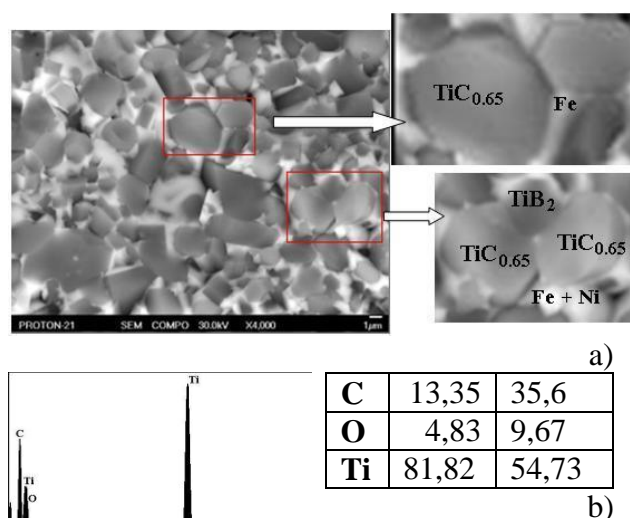
Based on the X-ray spectral analysis, the composite consists of the TiC phase and the TiB$_2$ phase. The results of X-ray spectral analysis indicate the presence of approximately 5-10atomic% of oxygen in the zone of the carbide grain location. Synthesis of titanium diboride and titanium carbide in a medium containing a residual amount of oxygen occurs with the formation of oxycarbides of variable composition containing up to 10% atomic of oxygen, located in the carbon vacancies of nonstoichiometric titanium carbide.

The excess amount of boron up to 20atomic%, detected as a result of local microanalysis, is located in the tetragonal interstices of the titanium diboride lattice. The introduction of a boron atom with a radius of 0,0875 nm into the interstice leads to an increase in both lattice periods *a* and *c* and the formation of titanium diboride of variable composition with lattice parameters a=3,0317, c=3,2274.

CERAMIC MATERIALS BASED ON ALN-Y$_2$O$_3$-C
FOR ELECTRONICS

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For using in electronics we obtained composite materials based on a blend made of AlN powder, Y$_2$O$_3$ and soot powders by the method of free sintering in a nitrogen atmosphere. The content of soot powders in the blend based on aluminum nitride was 5wt.%. A blend for manufacturing composite materials was mixed for 3 and 6 minutes, thereafter these composites were sintered at temperatures 1800 and 1850 °C. The structure of these ceramics were investigated by the method of SEM and by the X-ray analysis with using by the Rietveld method. The measurement of electromagnetic waves damping at frequencies of 34-36 GHz.

As shown calculation of the density of composites, some materials which were sintered at the temperature of 1850 °C had the higher of density (3.12-3.14 g/cm^3) than were sintered at 1800 °C. Results of the analysis showed that both materials had of main phases AlN (hexagonal and cubic), Y$_3$Al$_5$O$_{12}$, Al$_3$O$_4$ but the composite with a largest time of the blend mixing contains more of Al$_3$O$_4$ phase (3wt.%) than the composite with less grinding time (1wt.%). The structure of composites is presented as an aluminum nitride matrix with inclusions of carbon nanoparticles, with layers of Y$_3$Al$_5$O$_{12}$ placed along of grains boundaries and with local inclusions of Al$_3$O$_4$. The study of structure in the points of some phases showed that carbon presents not only as individual inclusions, but it also little presents in the AlN, Al$_3$O$_4$, Y$_3$Al$_5$O$_{12}$ grains. Results of measurements of electromagnetic waves attenuation at frequencies of 34-36 GHz of ceramics showed that materials which were mixed at 3 and 6 minutes had attenuation 6.5 and   7.6 dB, respectively.

The difference in the values of the damping of microwave radiation for materials were made from the compositions that were mixed at different times can be explained by the differences in the formation of the structures of the obtained ceramics. Thus, with increasing time of mixing and grinding of the blend, the specific surface of soot particles that were placed in the structure throughout the sample volume was increased, which in turn affected the increase of absorption of microwave radiation.

For samples of these ceramic materials were measured a specific electrical resistance which was about $(1-1.7) \cdot 10^{11}$ Ohm·m.

OPTIMIZATION OF STRUCTURE AND MECHANICAL PROPERTIES OF THE LISTED MULTICOMPONENT COMPOSITE OF THE Ti-B$_4$C-Fe-Ni SYSTEM OBTAINED BY THE HIGH-TEMPERATURE SYNTHESIS METHOD

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Modern high-tech branches of nuclear energy, machine building, electronics, defense industries are in dire need of new light refractory materials, high-hard, plastic, with a high modulus of elasticity.

The preparation of new refractory composites of the Ti-C-Fe-Ni system and the Ti-B$_4$C-Fe-Ni system by the self-propagating high-temperature synthesis of the initial powders allows simultaneously synthesizing a metal matrix composite in which titanium carbide in a boron-free system is enhanced by titanium diboride for a system with boron carbide the formation of a high-strength refractory skeleton in a ductile iron-nickel matrix.

The replacement of carbon by boron carbide in the eutectic composition of the initial powders results in intensive fragmentation of the synthesized carbide-boride framework of the composite obtained. The grain size of titanium carbide in the composite of the Ti-B$_4$C-Fe-Ni system decreases at least 5 times as compared to the system without boron, and contributes to the appearance of a more homogeneous structure.

According to the microhardness measurements using the nanomicroindentation method, the maximum microhardness values for the carbide-boride carcass range from 30GPa to 39GPa, which corresponds to the theoretical microhardness values for titanium carbide and titanium diboride at room temperature and 20-30% higher than the maximum microhardness values for a composite without boron. The minimum values of microhardness are determined mainly by the effect of the ductile iron nickel matrix and vary from 2 GPa to 10 GPa, depending on the composition.

Synthesized composites of the Ti-B$_4$C-Ni system, along with high hardness, also possess a high modulus of elasticity - up to 400 GPa, comparable with the theoretical strength characteristics of titanium carbides and diborides. It is these characteristics of armored ceramic materials, together with a relatively low density, that determine the high protective qualities of ceramics compared to metal armor of the same weight.

Based on the results of structural diffraction studies, the composite Ti-B$_4$C-Fe-Ni composite is a heterophase structure consisting of 80% of a superhard refractory carcass based on carbide and titanium diboride compounds and a plastic cement matrix consisting of solid solutions of iron and nickel. These experimental data are in complete agreement with the data of the thermodynamic analysis of the crystallizing refractory compounds of the Ti-B$_4$C-Fe-Ni system [Baglyuk G. and etc.]. Thermodynamic analysis shows that in the composite, one should expect the production of such stable refractory compounds as TiB$_2$ and TiC. The lowest free energy of formation is inherent in titanium carbide. And, consequently, in the process of self-propagation high-temperature synthesis, in the first place, TiC carbide grains with minimum values of free energy in the temperature range 1270-1870 ° K are formed. The formation of titanium diboride (TiB$_2$) occurs, probably, in the temperature range 1150-1400 ° K, where the free energy of formation of titanium diboride has negative values.

WETTING AND BRAZINING OF SUPERHARD MATERIALS

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Superhard materials (SHM) - diamonds, compositions based on dense modifications of boron nitride, due to a combination of unique properties, have been important in industry. SHM are produced in ultra-high pressure chambers and therefore their dimensions are limited. For use in practice, they must be fixed to the holders, housings by brazing. The wetting of SHM by the sessile drop method by metal multicomponent fillers which based on copper was investigated. Filler compositions for brazing of SHM were developed. The apparatus and method were described in [1, 2]. As objects of studying of SHM were selected CVD diamond, materials based on dense modifications of boron nitride BNsf (elbor-P, hexanite-P, composite 05-IT). The composites of metal powders (Cu, Sn, Pb, Ti, Ni) for filler bases were investigated. Before the wetting the surface of SHM was polished with a diamond tool up to roughness about 0.5 μm. The filler was pressed into tablets with Ø 2mm and height 2 mm. The samples of SHM with filler tablets on their surface were loaded into vacuum.

The wetting of materials based on BN_{sf} at different phase ratios of BN_{sf} and BN_v were studied at 850-950 °C, vacuum $2\text{-}3\cdot10^{-3}$ Pa. It was found that as the content in the samples of the BN_v phase increases, the wetting angle decreases. The chemical activity of BN_v phase to metal melts is greater than the for BN_{sf} phases. This factor this factor causes an improvement in wetting. The results are in good agreement with the IR reflection spectrum of BN-based polycrystals with different phase composition. The microstructure of the SHM-filler transition zone was studied in the characteristic emitting of metals which are part of the filler - Cu, Sn, Pb, Ti, Ni. It was established that Ti adsorbed on the BN_{sf} surface. Copper and other metals distributed uniformly in filler volume.

The titanium adsorption on the SHM surface improves the wetting of these materials.

A well-defined boundary between the filler and SHM, as well as between the filler and metal holder (steel, hard alloy), is not observed. In the process of formation of filler layer, the metals diffuse into each other, mixing them, the formation of mutual solid solutions and the subsequent joint crystallization. The composition of the filler for brazing of BN_{sf}-based materials (in % wt.) is 61Cu-19Sn-13Pb-6Ti-1Ni. The optimal temperature for brazing of BN_{sf}-based materials in vacuum is 950 °C, holding time is 2 min. The cutting tools for various purposes (through, undercut, boring, threaded, special) were manufactured by adhesively-active brazing. The wetting of CVD diamond samples (the size 10x10x1 mm) was studied at a temperature of 20-900 °C in vacuum furnace ($p = 5 \times 10^{-5}$ Pa). The filler composition for the brazing of CVD diamond was elaborated (in % wt.) 72.1Cu-18.0Sn-9.9Ti. It was shown that the holding time has a dominant effect on wetting process: after 2 min and at 850 °C the contact angle has decreased up to $\theta = 41$ deg., after 3 min up to $\theta = 38$ deg. At increasing temperature up to 900 °C the contact angle decreases up to $\theta = 27$ deg., at 900 °C and 1 min. - $\theta = 7$ deg. The elaborated filler was used at fabrication of pass-through turning tools: CVD diamond plates was brazed to the steel body-holder of the turning tool.

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THE PROPERTIES OF ZTA POWDERS, PRODUCED BY THE HYDROTHERMAL METHOD IN AN ALKALINE MEDIUM

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Composite materials in the $Al_2O_3 - ZrO_2$ (Y_2O_3, CeO_2) system belong to a new class of materials, where high values of mechanical properties are due to the cumulative effect of the Al_2O_3 matrix and ZrO_2-based solid solution as the reinforcing phase (ZTA). There are several toughening mechanisms in ZTA - composites: transformation toughening mechanism, deflection (branching) of cracks and modular load transfer. ZTA is widely used as structural and medical materials for various purposes.

It is known that the materials properties depend on the properties of the starting powders. Powder properties are determined by the method of synthesis. Aluminum oxide is characterized by a large variety of polymorphic modifications. In this work, the powders were synthesized by the hydrothermal method in an alkaline medium, in order to study the synergetic effect of Al_2O_3 and solid solution based on ZrO_2 phase transformations.

Four compositions of nanocrystalline powders were synthesized, where Al_2O_3 content varied from (wt.) 90 % to 58.5 % and the ZrO_2-based solid solution content, respectively, from (wt.) 10 % to 41.5 % (AZ90, AZ80, AZ70, AZ58). The zirconium-based solid solution composition is (% mol.): 90 ZrO_2-8CeO_2-2Y_2O_3. $ZrOCl_2$ and metals nitrates were used as starting materials.

According to the thermogravimetry results, the basic weight loss in the samples was determined both by the removal of adsorbed bound moisture and by the decomposition of aluminum hydroxides, which were formed during hydrothermal synthesis. In addition, the process was accompanied by the crystallization of X-ray-amorphous ZrO_2 (Y_2O_3, CeO_2), which was formed during hydrothermal synthesis.

According to the XRD results it was determined that boehmite γ-AlO(OH) and low-temperature metastable cubic solid solution based on ZrO_2 (F-ZrO_2) were formed after hydrothermal synthesis in alkaline medium.

The morphologies of the composite powders are shown in Figure 1. The shape of the agglomerates changed with the increasing the content of a solid solution based on ZrO_2. In the AZ90 powder soft round-shaped agglomerates from 2 to 10 microns, (several 20 microns) were formed (Figure 1a). There were dense agglomerates from 2 to 20 microns in the AZ58 powder, besides, multilayer agglomerates up to 40 microns were noted (Figure 1 b).

The obtained results are constitute the scientific basis for microstructural design of ZTA-composites.
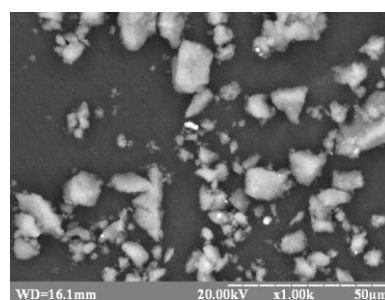
(a)
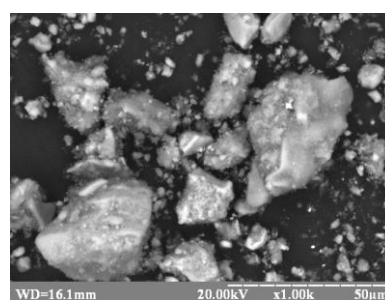
(b)

Figure 1 – The morphologies of powder AZ90 (a) and AZ58 (b).

EFFECT OF BORON ON THE PHASE COMPOSITION, STRUCTURE, AND PROPERTIES OF IRON-IMPREGNATED FRICTION MATERIALS

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Friction composites made by powder metallurgy should have a heterogeneous structure formed by a mixture of crystals of different hardness. In the case of friction, less solid crystals are destroyed first, as a result of which the friction surface of the material decreases and the lubrication conditions of the latter improve. Such properties are possessed by iron-glass composites, which include boron carbide. Boron carbide is a very hard, refractory and inert substance.

In the present work, studies of the phase composition, microstructure, and physical-mechanical properties of Fe-2%B_4C-5%glass composite (BN, Cu) obtained by sintering at temperatures of 1100-1200^{0}C followed by stamping at T=1050-1100^{0}C are presented.

The microstructure of the metal base is a eutectic with a plate morphology with evenly distributed inclusions of FeB borides with a microhardness of 20 GPa. It has been established that thin eutectoid plates are Fe_2B (15 GPa) boride. At the boundaries of the glass inclusions and the metal matrix, there are sections of a large extent enriched with copper and areas of borocementite (9-11 GPa). Inside the glass inclusions, fine-dispersed light inclusions of copper and carbides (8 GPa) are revealed, Fig.1a.

Studies of the X-ray diffraction structural analysis of iron-glass composites have shown that the metal matrix retains a body-centered lattice, as well as boroncementite $Fe_3(B_{0,7}C_{0,3})$ and borides Fe_2B, FeB are formed, as evidenced by the appearance of the corresponding lines on the radiogram, Fig.1b.
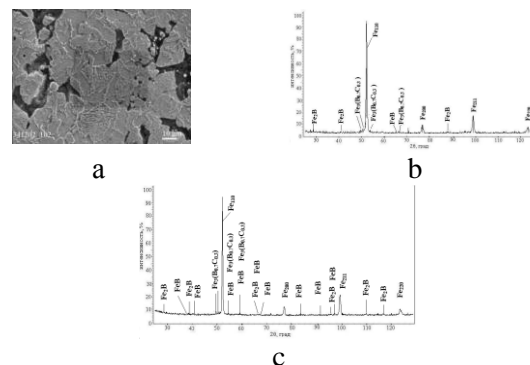
Fig.1. Morphology of metal-glass composites Fe-B_4C-glass (BN, Cu): a-microprobe image in COMPO mode, diffraction patterns (b-T=1100^{0}C, c-T=1200^{0}C).

When the sintering temperature increases to 1200^{0}C with subsequent stamping at 1100^{0}C the number and intensity of the lines increases, Fig.1c. This increases the microhardness of the metal matrix. The increase in the microhardness of the material during sintering and the intensity of the boride lines can be explained by the additional formation of borocementite due to diffusion in the austenite regions enriched in carbon. During sintering, the amount and dimensions of Fe_3C cementite increase due to dissolution of boron atoms in the last and the formation of borocemintite $Fe_3(B_{0,7}C_{0,3})$. The microhardness of the borides themselves varies with their composition, in particular, on the ratio of iron and boron. The stability of the grain structure increases; at high temperatures (1100-1200^{0}C) the entire boron goes to the formation of borides and a new FeB boride is formed. At the same time, the microhardness of the metal matrix to 5 GPa and borides up to 22 GPa is maximized.

INVESTIGATION OF ZrN-ZrB$_2$ COMPOSITION SYNTHESIS BY SPS METHOD

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ZrN-ZrB$_2$ composition can be used for the manufacture of parts of jet engines, armored plates, parts of hypersonic aircraft, cutting tools, crucibles, electrodes for plasma arc devices due to the fact, that its compounds have a number of unique properties [1].

The initial ZrH$_2$+BN mixture of powders was used for the purpose of synthesizing the ZrN-ZrB$_2$ composition containing 35 wt. % ZrB$_2$. Sintering was carried out using a pulsating current on the Dr. Sinter® 1050 arrangement in a vacuum of 10-60 Pa. There was no exposure at sintering temperatures of 900-1500ºC, the exposure was 3 min at 1600-1900ºC.

During sintering, gas evolution was observed in the interval of T=520-1500°C. The first significant peak on the curve of the residual pressure in the chamber versus the sintering time was observed at 650-680°C. According to [2], this could be due to the decomposition of a partially hydrated B$_2$O$_3$ oxide layer located on the BN surface. This layer consisted of H$_3$BO$_3$ and decomposed by endothermic reactions. The presence of the second small peak at T=700°C was associated with the start of the dehydrogenation process, which was also endothermic. The peaks in the power curve versus time, that accompanied the gas evolution peaks, confirmed the endothermicity of the above processes. During the heating to T=900°C, dehydrogenation led to the transition of the ZrH$_2$ dihydride into hydride phases with a lower hydrogen content (ZrH$_{1,66}$, ZrH, ZrH$_{1,801}$), ZrB$_2$, ZrO$_{0,35}$ and ZrC$_{0,32}$H$_{1,20}$ phases formation.

When heated to T=1100°C, activation of carbon diffusion into the crystal lattice of hydrides occured with an increase in the relative amount of zirconium carbohydride ZrC$_{0,32}$H$_{1,20}$, and dehydrogenation took place with a decrease in the hydrogen content in the sample. Dehydrogenation was accompanied by a small wide 3rd peak (T=1020-1030°C) on the curve of the residual pressure in the chamber versus time. There was also the formation of ZrN and an increase in the relative amount of ZrO$_{0,35}$. When heated to T=1300°C, zirconium carbohydride ZrC$_{0,32}$H$_{1,20}$ decomposed, ZrC carbide was oxidized with residual oxygen, zirconium was reduced from ZrO$_{0.35}$ oxide, further dehydrogenation and the formation of zirconium nitrohydride ZrN$_{0,4}$H$_{1,10}$ occured. At T=1100°C, a sharp increase in the residual pressure in the chamber began due to the large amount of evolved gases. The maximum of the 4th largest peak was reached at T=1370-1380°C. Heating to T=1500°C led to the decomposition of zirconium nitrohydride with the formation of ZrN. As a result, ZrN+ZrB$_2$ composition was formed with a small residual impurity of the original boron nitride. Sintering at T=1600-1700°C with a holding time of 3 min did not completely eliminate the residual BN. An increase of temperature to 1800-1900°C led to the obtaining of the composition without impurities.

According to electron microscopy data at 1100-1500°C, fairly large nonuniform inclusions of 50-100 μm in size were observed on the surfaces under study, which tended to decrease with increasing of sintering temperature. In all likelihood, these inclusions were loose, unsintered regions of samples with a high content of unreacted phases (ZrC$_{0,32}$H$_{1,20}$, ZrH and BN at 1100°C, ZrN$_{0,4}$H$_{1,10}$ and BN at 1300°C), or a region of reduced density of the ZrN-ZrB$_2$ at 1500°C. At the sintering temperatures of 1700-1900°C, the regions with a reduced density of ZrN-ZrB$_2$ composition had a size of 5-20 μm.

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STRUCTURE AND MICROHARDNESS OF THE CARBOCHROME COATING ON STEEL

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The increased performance characteristics of products, in particular their wear resistance, depend largely on the microstructure of the surface and the hardness of the materials from which they are made. The paper presents the research results 40X and 65Gsteel samples with carbochrome coatings obtained by their thermochemically processing.

Samples for carbochroming were prepared by their carburization at a temperature of 900-920 °C and subsequent their chrome plating at 800-1100 °C. This makes it possible to obtain coating samples up to 1 mm thick. The formation of coatings was ensured by successive saturation first with carbon, and then with chromium. This has resultedan increase in not only the hardness and wear resistance of samples, but also their heat and corrosion resistance.

The microhardness was measured by the Vickers method on the PMT-3 device. The structure of the sputtered samples was analyzedby metallography. These studies have shown that structural changes occur both on the surface layers of the substrate and inside the carbochrome layer during thermochemically processing. Such changes determine the value of microhardness, which depends on the location of the indenter on the surface of the samples and on the magnitude of the load. These data are shown in Fig. 1 and correspond to an increase in the microhardness from the substrate to the surface of the coating.

For coatings, the transition zone between the substrate and the coating does not contain any sharp transition zones and, with the coating thicknesses studied, its microhardness is practically unchanged when removed a distance of up to 1 mm from the substrate, which ensures a long-term service life of the products.
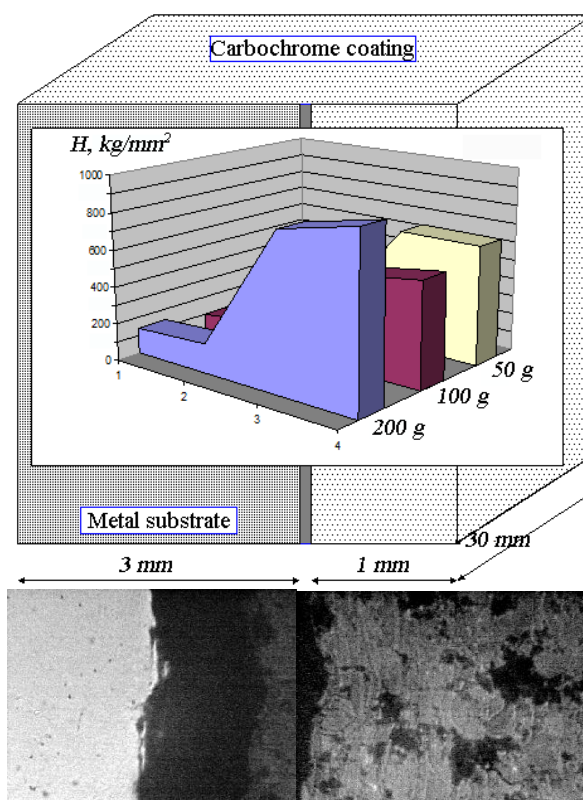
Fig. 1 - Microhardness and structure of the carbochrome layer in the sections of the 40X steel sampleat various loads

КЕРАМИКА НА ОСНОВЕAlB$_{12}$C$_2$

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Boron carbide is the most studied and widely used material in the family of refractory compounds based on boron icosahedra. Its more correct chemical formula may be represented as $B_{15-x}C_x$,leading at x=3to $B_{12}C_3$,or more conventional B_4C, which does not reflect its structural specifics.Boron carbide's extreme properties are very well known, especially after the review in [1] was published. This review also shows the drawbacks of B_4C, the main two being high fragility (K_{1C}around 1,5 MPa·m$^{1/2}$)and hot-pressing temperature of 2200-2300 °C. The task of modern materials science is to improve technological and mechanical properties of boron carbide by the modification of a linear chainof carbon atoms -C-C-C- that connects boron icosahedra B_{12}. Ternary aluminium dicarbododecaboride, a structural analogue of boron carbide, may be considered as such a compound. It is expected, that introducing Al atoms as a metallic component into the carbide bonding -C-C-C- will increase mechanical properties of B_4C.

The aim of the work was to develop the basic conditions of interaction between boron carbide an aluminium and study the phase formation in the B_4C– Al system in a broad range of aluminium concentrations.

An interaction in which all carbon in B_4C is substituted by aluminium atoms was chosen as a basic reaction:

$$B_{12}C_3 + 5Al \rightarrow AlB_{12} + Al_4C_3 \ (1).$$

Thermodynamic calculations show the possibility of such reaction with large reduction of the system's internal energy. But, as it turned out in practice, it does not proceed to the end in the temperature range up to1400 °C, probably due to entropy influences. Maximum aluminium content is as in (1). The products in this case, as determined from XRD data using Rietveld full profile analysis, are: $AlB_{12}C_2$ ($AlB_{40}C_4$), $Al_8B_4C_7$, Al_3BC, Al. Aluminium-reach phases might be inclined to hydrolysis and have low melting points. Therefore,AlandAl_3BCwerechemicallyremoved.Th eratiobetween$AlB_{12}C_2$ (a=5,6739 nm; c=12,4669 nm)and$Al_8B_4C_7$ (a=5,9174 nm; c=15,9245 nm)phasesafterchemicaltreatmentis87 % to 13 % bymassinabroadrangeofaluminiuminitialconcentrat ions. If its amount is substantially reduced, some amounts of AlB_{10} ($AlB_{24}C_4$) and unreacted B_4C may also be discovered in the synthesis products.

The figure shows a microphotograph of the polished surface of two-phase material. Non-icosahedral $Al_8B_4C_7$allowed to activate the hot-pressing process: its temperature did not exceed 1900 °C. The material's microhardness at 2,5 N, determined using PMT-3, was 27 GPa.
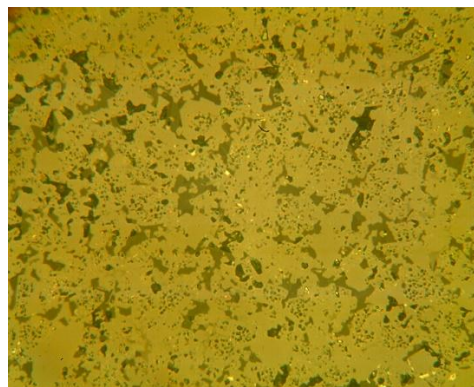
Figure–Microphotograph (x800) of the material's surface

The method of synthesis developed here allows the modification of -C-C-C-chain by aluminium and produces aluminium dicarbododecaboride$AlB_{12}C_2$ as the main phase.The second phase$Al_8B_4C_7$activates hot-pressing and lowers its temperature.

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ПОЛУЧЕНИЕ И ИССЛЕДОВАНИЕ СЛОИСТЫХ ВАКУУМНЫХ КОНДЕНСАТОВ НА ОСНОВЕ ТУГОПЛАВКИХ СОЕДИНЕНИЙС ИЗМЕНЯЕМЫМ СОСТАВОМ БИСЛОЯ

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Синтез и фундаментальные исследования наноразмерных нитридных покрытий являются актуальным и востребованным направлением развития нанотехнологий и модификации материалов. Более десяти лет вплоть до настоящего момента широко исследованы и применяются многоелементные (тройные) нитридные соединения, такие как TiAlN. Одним из путей дальнейшего совершенствования системы TiAlN является увеличение количества легирующих элементов. Для этого могут быть использованы такие элементы какSi, Y, V, Cr и другие. При этом формирование слоистой структуры делает возможным получение систем с уникальными трибологическими и прочностными характеристиками путем комбинирования слоев с разными свойствами, а также за счет процессов на границе раздела фаз.

Многослойные покрытия (TiAlSiY)N/CrN, (TiAlSiY)N/ZrN, и (TiAlSiY)N/MoN были получены методом вакуумно-дугового осаждения на модернизированной установке «Булат – 6» [1]. В качестве материала подложек использовалась сталь 12×18H9T (аналог сталей SUS321 и 321S51) с размером образцов 18×20×2 mm^3.Давление рабочей (азотной) атмосферы в камере осаждения (P_N) составляло $P_N = 4*10^{-3}$ Торр. На подложку подавался постоянный отрицательный потенциал -U_b = -110 В

Результаты ренгеноструктурного анализа указывают на формирование гетерофазногосостава в соответствии с бислойной композицией, однако для многоелементных слоев (TiAlSiY)N/CrN покрытия регистрируются включения фазы AlN. В то время, как преобладающая фаза в многоелементном слое формируется путем изоморфных замещений легирующими атомами в ГЦК-решетки TiN.

Испытания твердости (H) и измерение приведенного модуля упругости (E*) проводились с учетом глубины нагрузки и с использованием нанотвердомера Hysitron TriboIndenter 950. Максимальные значения нанотвердости и модуля упругости, 35,9 ГПа и 406,8 ГПа, соответственно, получены для системы (TiAlSiY)N/MoN и достигаются на разной глубине измерения. Аналогичные значения дляпокрітий(TiAlSiY)N/CrN (23.4 GPa и 300.2 GPa) и (TiAlSiY)N/ZrN (22.1 GPa и 271 GPa) значительно уступают приведенным выше значениям, однакосопоставимымеждусобой. Отличие в фазово-структурномсостоянии, в частности изменение размеров кристаллографического зерна в сторону укрупнения,определилоразличие в механическихсвойствахпокрытий.

Известно, что кроме твердости и модуля Юнга, важной характеристикой свойств функциональных покрытий являются соотношения H/E^* и H^3/E^{*2}. Высокое значение H/E^* означает уменьшение контактного давления, так как приложенная нагрузка распределяется на большую площадь. Поэтому, покрытия с высокими значениями H/E^* ($H/E^* \geq 0,1$) демонстрируют высокую износостойкость и рекомендованы к промышленному использованию. Рассчитанные значения H/E* и H3/E*2для (TiAlSiY)N/MoN покрытия составили $\simeq$ 0.09 и 0.3 соответственно. Наблюдается незначительное снижениерасчетных соотношений для (TiAlSiY)N/CrN ($\simeq$ 0.08 и 0.14) и (TiAlSiY)N/ZrN ($\simeq$0.09 и 0.15).

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HEAT-RESISTANT MATERIALSOBTAINED BY SHS-ELECTRIC ROLLING

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As it is known from the investigations, during self-propagating high temperature synthesis as a result of SHS thermal impulse an exothermic chemical reactions begins and combustion wave front relocates at a certain speed in the mixture of reagents. SHS is a rapid process. Combustion phase duration varies between 0,5-15 sec. This limits the range of heat pressure processing of material. Based on the above during the compaction of the product, in order to ensure its homogenous qualities, it is necessary to ensure isothermal regime of its hot pressure processing, which is only possible during joined, combined process of SHS and pressure processing. With the existing technologie by pressure processing it is possible to manufacture product with such dimensions, where SHS (before the pressure processing) ends in maximum of 15 seconds. The continuous progress of the process can be achieved by the suggested, innovative, inexpensive, energy saving, combined technological process of self-propagating high temperature synthesis and electric rolling. It is the only process from existing technologies that provides the continuity of SHS and billet's hot deformation (rolling) process, compensation of heat losses and manufacturing of products with demanded longitudinal dimensions.The principle of working with this method is following: the container filled with pre-compacted charge is supplied to rolls of special rolling mill, a slight biting occurs. Rolls stop. Passing the contact between the container and rolls electric energy is supplied into deformation zone. Produced joule heating combusts the compacted charge in initial section of deformation zone and initiates SHS process. While obtaining compact synthetic composite ceramic material by SHS-Electric Rolling, it is most important to select optimal technology parameters. These parameters are the time and pressure characteristics. After correct selection of these characteristics the authors obtained compacts in the Ti-B-N-Me and Ti-B-N-C-Me systems with the following characteristics: they are practically non-porous materials, the porosity - 0,4% and 1,2% respectively, hardness - 91,5-92,5 HRA and 92,3-93,3HRA respectively, density - 4.3-4,4 g/cm^3 and 4,5-4,7 g/cm^3 respectively (with porosity - 0,4% and 1,2%, hardness - 91,5-92,5 HRA and 92,3-93,3HRA, density - 4.3-4,4 g/cm^3 and 4,5-4,7 g/cm^3 respectively). These materials resist once-only (single) dynamic impact possessing energy 18000-20000 joules, with the weight of manufactures 68-65 kg/m^2 (6,8-6,5 g/cm^2).

The knowledge of regularity of transformation of initial components into a final product allows identifying not only the optimal composition and the technological parameters for obtaining the materials, but also we can forecast exploitation properties of these materials.

It can be predicted that while penetrating the destroying energy indenters in materials of above mentioned systems, at first stage there is a crash of pillar/needle type grains. Those grains have higher hardness than the spherical grains on the base of TiN and TiCN phase. Those spherical grains itself have higher viscosity and plasticity than the grains of TiB_2 phase. While crashing the pillar/needle type grains there is accumulation of portion of destroying energy, though at the first stage there is no disorganization of TiN and TiCN phases, as they are characteriszed with higher viscosity and plasticity. As a result we have delayed crack formation and crashing, which provides the crach-resistance and increasing the lifetime of product.

INFLUENCE OF HIGH PRESSURE AND TEMPERATURE ON INTERACTION IN THE TiB$_2$-TaB$_2$ SYSTEM AND PHYSICO-MECHANICAL PROPERTIES OF OBTAINED COMPOSITES

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The preparation of solid solutions based on transition metal diborides ofIVa, Va groups at high pressures is interesting from two points of view: first, they have higher physico-mechanical properties than binary compounds; secondly, it is tempting to use such an effective method of consolidating powders as high static pressures to obtain them.Sintering powders of these diborides at high pressures allows without the use of activating additives to obtain highly dense ceramics and most fully realize the potentially high properties of these compounds in finished products. Such ceramics have a combination of increased hardness and reduced brittleness due to the fine-grained structure of the material [1, 2]. Itisknownthatasthealloyisenrichedwithboridewithlesssstrongbonds, thegrainsarereduced [3].According to our studies on sintering powders thereof under high pressure [2], titanium diboride is the highest hard and niobium, zirconium and especially tantalumdiborides have the highest ductility,and tantalum diboride of which has a higher hardness.

In comparison with other metal diborides of these groups, the difference in atomic radii of titanium and tantalum is minimal and amounts to only 2%. Unlimited mutual solubility of these diborides at a temperature of 3000 ° C is noted in [4]. According to [5], in the TiB$_2$-TaB$_2$ system, the formation of a continuous series of solid solutions occurs even at a temperature of 1300 ° C.

The interaction of the TiB$_2$ and TaB$_2$ phases at high pressures up to 4 GPa and temperatures up to 1900 ° C, leading to the appearance of depleted by boron of Ta$_3$B$_4$phasealong with a decrease in the lattice parameters of the TaB$_2$ phasewas revealed in [6]. Atthepresenttime, thepropertiesofmaterialsbasedonthemarepractically notstudied.

X-ray diffraction analysis was used to study the interaction in the TiB$_2$-TaB$_2$ system during the sintering of powder mixtures of various compositions

at pressures of 2.5 and 4 GPa in the temperature range 1500-1900 ° C with a holding time of up to 15 min and the effect of sintering regimes on the hardness *HV1* and the fracture toughness$K_{1C}$of the resulting composites.

The best combination of physico-mechanical characteristics (*HV1*=22.9±0.7 GPa, K_{1C}=7.7±0.6 MPa.m$^{1/2}$) was obtained for samples sintered at a pressure of 2.5 GPa and a temperature of 1900 ° C.

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ФИЗИКО-МЕХАНИЧЕСКИЕ СВОЙСТВА МИКРО-/ НАНОКОМПОЗИТОВ НА ОСНОВЕ НИТРИДА КРЕМНИЯ, СПЕЧЕННЫХ ПРИВЫСОКОМ ДАВЛЕНИИ

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Нанокристаллические материалы на основе нитрида кремния представляют интерес в связи с ожиданием их болеевысоких физико-механических свойств и термической стабильности. Обычным спеканием и горячим прессованием трудно получить плотные материалы на основе нитрида кремния без активаторов и наноразмерную структуру. Кодному из наиболее перспективных методов, позволяющих формировать такуюнанокристал-лическую структуру материала относят плазменно-искровое спекание в графитовых пресс-формахпод давлением.Термобарическая обработка при высоком давлении (HPS), также является одним из эффективных методов формирования плотной нанозеренной структурыматериала за счет интенсификации спекания и сокращения времени процесса.

Целью работы являлось исследование возможности получения нанокомпозитов на основе нитрида кремния с повышенными физико-механическими свойствами. В качестве исходных компонентов использовались смесимикропорошка α-Si_3N_4 марки LC-12 (1 мкм, «H.C.Starck», Германия) печного синтеза инанопорошка α-Si_3N_4 (20-40 нм, «Neomat Co», Латвия) плазмохимического синтеза в пропорции 1:1, которые затем смешивали с нанопорошками оксидов со средним размером частиц 20-40 нмв

необходимомсоотношении в барабанном смесителе в течение 20 ч. После смешивания порошки гранулировали протиркой через сита с размерами ячеек 315 и 100 мкм. Составы указаны в табл.1.

Таблица 1 — Составы исходных смесей на основе нитрида кремния

Шифр смеси	Состав смесей, масс. %			
	α-Si_3N_4, (Starck)	β-Si_3N_4, (Neomat)	Y_2O_3	Al_2O_3
2-SSN	45	45	5,7	4,3
3-SSN	42,5	42,5	8,55	6,45

Спекание композитов проводили в устройстве высокого давления типа наковальни с углублениями при давлении 4 ГПа в интервале температур 1500-1800 °C. Время спекания 1 мин.

Получить компактные образцы состава 3SSNудалось только при температурах 1600-1700 °C.Однако они имели значительно более низкую плотность и микротвердость (10,8-16,7 ГПа), чем у образцов 2SSN (табл. 2), но более высокую трещиностойкостьK_{1C}(7,3МПа·м$^{1/2}$).

Полученные керамические нанокомпозиты состава 2SSN, спеченные в оптимальных режимах,имеют микротвердость 26,5-33,8 ГПа, твердость по Виккерсу$HV1$20,5 ГПа, трещиностойкостьK_{1c}6,5-6,8 МПа·м$^{1/2}$ и модуль Юнга 287-299 ГПа.

Таблица 2 — Свойства нанокомпозита 2SSN

Номер образца	$T_{сп.}$, °C	Плотн ость, г/см^3	Теплопров одность, В/м·К	Уд.электр. сопротивление, Ом·см	Микро-твердость, ГПа, (нагр. 1,5 Н)	Модуль упругости, ГПа	Коэф. Пуас-сона
2-SSN-2	1500	3,192	17,97	$1,9 \cdot 10^{14}$	$31,2 \pm 3,2$	286 ± 5	0,22
2-SSN-3	1600	3,181	18,21	$1,5 \cdot 10^{15}$	$33,8 \pm 4,7$	299 ± 3	0,25
2-SSN-5*	1700	3,168	20,45	$2,3 \cdot 10^{15}$	$26,5 \pm 2,1$	287 ± 3	0,27
2-SSN-4	1800	3,165	17,82	$2,7 \cdot 10^{15}$	$21,1 \pm 3,9$	281 ± 4	0,28

NICKEL ALLOYING WITH MOLYBDENUM BY ELECTROLYSIS OF FLUORIDE-BORATE MELTS

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The basic theses of the galvanic diffusion saturation theory suggest the possibility of control of the composition (solid solutions, intermetallide phases, saturated metal layers etc.) and the thickness of diffusion coatings by changing the electrolysis parameters.

A method for galvanic diffusion molybdenumation from a fluoride-borate electrolyte is developed with the following technological parameters: electrolysis temperature increase up to 1000÷1050 °C; electrolyte composition based on KF-B_2O_3 ($K_2B_4O_7$) containing up to 10 mol. % MoO_3; cathode current density 0.005÷0.100 $A \Box cm^{-2}$; application of reversive current mode of electrolysis.

Depending on the conditions of electrolysis, five types of deposits were obtained: adherent solid deposits; adherent solid deposits overgrown with dendrites; dendritic deposits; adherent solid deposits passing into inadherent; adherent solid deposits simultaneously passing into inadherent and dendritic ones.

To determine the composition of the electrolyte for the production of adherent continuous coatings, cathode products of the electrolysis of the KF-B_2O_3-MoO_3 systems of various compositions were studied. Electrolysis was carried out at 1000 °C with cathode current density 0.05 $A \Box cm^{-2}$ using mo-lybdenum anode. According to X-ray diffraction analysis, all deposits consisted of metallic molyb-denum. Only dendritic precipitates were obtained in KF-MoO_3 melts. When B_2O_3 or $K_2B_4O_7$ additi-ves were added to the melt, solid deposits were deposited passing over time into inadherent or den-dritic ones. The optimum electrolyte proved to be of the composition KF (65 mol.%) − B_2O_3 (30 mol.%) − MoO_3 (5 mol.%) which was used later to study the effect of electrolysis parameters on the composition and properties of deposits.

At 1000 °C, adherent solid deposits were ob-tained within the current density range 0.03÷0.08 $A \Box cm^{-2}$. The current yield is 85-99%.

Molybdenum placed into the studied melt is subject to general corrosion at a rate $(1.5÷3.5) \Box 10^{-7}$ cm/s. The cathode weight change differs from the calculated by Faraday law from the amount of molybdenum mass loss without current. This suggests that the current yield deviation from the calculated theoretically is due to the chemical corrosion of a part of the precipitated molybdenum.

The galvanic diffusion molybdenumation of nickel in melts of various compositions have shown a nonlinear dependence of the weight change on the current density and the electrolysis duration. This is associated apparently with the phase composition change of the surface layer. The results of metallographic, micro-X-ray, and X-ray phase analysis of the surface layer confirm this assumption. During the electrodeposition process, one can distinguish three time regions: the formation of a solid solution of molybdenum in nickel; formation of the intermetallic Ni-Mo phase; and growth of solid molybdenum coating.

On the potential-time curves, four time regions of the potential change could be found:

1. the potential growth over time − the formation of a solid solution of molybdenum in nickel, and the molybdenum concentration increase in it;
2. the potential stability over time − the surface appearance of the Ni-Mo phase nuclei solid solution;
3. the further potential increase − the intermetallic layer growth and the concentration increase in it;
4. the potential stability over time − the maximum molybdenum concentration achievement in the intermetallic compound, the molybdenum phase formation, and its growth.

HIGH-TEMPERATURE ELECTROCHEMICAL SYNTHESIS OF COMPOSITE MATERIALS BASED ON GADOLINIUM AND SILICON

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In accordance with the current-voltage dependences recorded in KCl-NaCl-CsCl melt at a tungsten electrode, the gadolinium ions reduction wave appears within the range of potentials -(2.3-2.4) V. When potassium fluorosilicate is added up to concentration of about $5.2 \cdot 10^{-4}$ mol/cm^3, a wave is observed on the voltammogram attributable to electroreduction of fluorosilicate ions within the potential range -(1.4-1.7) V.

High-temperature electrochemical synthesis of gadolinium silicides was carried out in purified and dried argon atmosphere; the cathode was tungsten, and the anode was a glass-carbon crucible. The process was carried out in molten NaCl-KCl-GdCl$_3$-K$_2$SiF$_6$ mixture at 973 K and in molten NaCl-KCl-CsCl-GdCl$_3$-K$_2$SiF$_6$ mixture at 823 K. Electrosynthesis of gadolinium silicides was carried out in potentiostatic mode, since it is the voltage that determines and controls the course of the deposition reaction.

To determine the optimum concentrations of GdCl$_3$ and K$_2$SiF$_6$, it should be taken into account that, during the first stage of electrosynthesis, silicon, as more electropositive component, is deposited. The gadolinium ions electroreduction begins with the consumption of potassium fluorosilicate.

The dependence of the cathodic deposites composition on the potassium fluorosilicate content in electrolytic bath was studied. The silicide phase appears in the cathode deposit with molar ratio GdCl$_3$: K$_2$SiF$_6$ = 1 : 1 in the chloride melt. Depending on the electrolyte composition and the electrosynthesis parameters, the GdSi$_2$ silicide phase and various phases mixtures, including Gd$_5$Si$_3$, were formed.

To find the optimal composition of the electrolytic bath, the following considerations were taken into account: firstly, the value of the limiting current of the electropositive component (silicon) deposition should be low, since in this case the value of the gadolinium deposition potential is reached; secondly, the current density and temperature are of great importance in the electrochemical synthesis.

The optimum electrosynthesis process duration for the GdSi$_2$ phase obtaining is $60 \div 90$ min. In general, the gadolinium silicides electrosynthesis process is determined by the following interrelated parameters: the electrolytic bath composition, the electrolysis duration, the voltage at the bath, and the temperature.

On the based of the aforementioned, the gadolinium silicides electrosynthesis can be represented in the following sequential steps:

– electroreduction of silicon ions;

– electroreduction of gadolinium ions at the preliminarily deposited silicon surface;

– interaction between deposited gadolinium and silicon at the atomic level with the formation of phases with different composition.

The electrochemical processes occurring during the gadolinium silicides formation can be represented by the following equations:

$$\text{SiF}_{4-x}\text{Cl}_x + 4e \rightarrow \text{Si} + (4-x)\text{F}^- + x\text{Cl}^- \qquad (1)$$

$$\text{GdCl}_{6-y}\text{F}_y^{3-} + 3e \rightarrow \text{Gd} + (6-y)\text{Cl}^- + y\text{F}^- \qquad (2)$$

$$q\text{Si} + p\text{Gd} \rightarrow \text{Gd}_p\text{Si}_q \qquad (3)$$
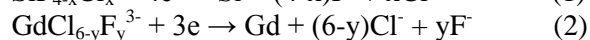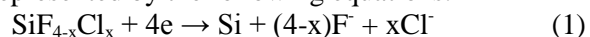
The single-phase GdSi$_2$ product yield was 0.3-0.4 g·A^{-1}·h^{-1}. The specific surface area of the fine GdSi$_2$ powders was 4.1-8.3 m^2/g.

Using laser diffraction analysis and scanning electron microscopy, the particle sizes of synthesized gadolinium silicide powders were determined. It was shown that the fraction of gadolinium silicide particles with a size of less than 100 nm was $50 - 65\%$.

HIGH-TEMPERATURE ELECTROCHEMICAL SYNTHESIS OF COMPOSITE MATERIALS BASED ON GADOLINIUM AND BORON

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The results of the study of the joint electro-reduction of gadolinium ions and fluoroborate ions have shown that the first wave observed at potentials -(1.4-1.5) V corresponds to the deposition of elementary boron, and the second, at potentials -(1.6-1, 8) B, corresponds to the process of reduction of gadolinium ions on a predeposited boron. The latter process is accompanied by the formation of gadolinium boride phases of various compositions. The depolarization occurring with gadolinium de-position can be explained by the interaction of gadolinium with boron. The third wave corresponds in our opinion to the deposition of pure gadolinium onto gadolinium boride at potentials -(2.2-2.3) V.

Similar studies were carried out in a NaCl-KCl-CsCl melt at a temperature 823 K. If melt contains only gadolinium chloride, one-stage electroreduction of chloride complexes to metal gadolinium takes place. The introduction of potassium fluoroborate into $GdCl_3$ containing melt causes the appearance of a wave of electroreduction of boron ions at potentials -(1.5-1.8) V on a volt-ampere curve. With the potassium fluoroborate concentration increase at constant concentration of gadolinium chloride, waves of electrochemical reduction of fluoroborate ions and of gadolinium chloride complex ions are fused on the current-voltage curve with formation of gadolinium boride phases of different composition.

High-temperature electrochemical synthesis of gadolinium borides was carried out in purified and dried argon atmosphere; tungsten was served as cathode, and glass-carbon crucible – as anode. The process was carried out in molten mixtures NaCl-KCl-$GdCl_3$-KBF_4 at 973 K and NaCl-KCl-CsCl-$GdCl_3$-KBF_4 at 823 K.

Electrosynthesis of gadolinium borides was carried out in the potentiostatic regime, since it is the voltage that determines and controls the course of the deposition reaction.

To determine the optimal concentrations of $GdCl_3$ and KBF_4, it should be noted that, during the first stage of electrosynthesis, boron, as more electropositive component, is deposited. Electroreduction of gadolinium ions begins with consumption of potassium fluoroborate.

The dependence of the cathode deposits composition on the content of potassium fluoroborate in an electrolytic bath was studied. The boride phase appears in the cathode de-posit with molar ratio $GdCl_3$: KBF_4 = 1 : 1 in the chloride melt. The boride phases content in the cathode deposit increases with the increase of the concentration of potassium fluoroborate in the melt. With molar ratio $GdCl_3$: KBF_4 = 1 : 3, gadolinium hexaboride is formed. The optimum duration of the electrosynthesis process for GdB_6 phases obtaining is about $60 \div 90$ min. In general, the gadolinium borides electrosynthesis process is determined by the following interrelated parameters: the electrolytic bath composition, the electrolysis duration, the voltage at the bath, and the temperature.

The single-phase GdB_6 product yield is 0.25-0.35 $g \cdot A^{-1} \cdot h^{-1}$. The specific surface values for finely dispersed GdB_6 powders were within 4,5-9,0 m^2/g range.

A number of studies have been performed enabling us to determine conditions under which nanosized powders of boride phases can be obtained. Using laser diffraction analysis and scanning electron microscopy, the particle sizes of synthesized gadolinium boride powders were determined. It was shown that the fraction of gadolinium boride particles with a size less than 100 nm was 40-60%.

THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIUM IN ALLOYS OF THE SYSTEM Ge–Yb

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Alloys of REM with p- and d- metals exhibit the following properties: magnetic, super- and semiconducting, high and low melting points, and the like. To optimize the conditions for their production, it is desirable to know the thermodynamic properties of phases and alloys, as well as the associated phase diagrams of the systems.

The phase diagram of the Ge-Yb system has been studied and constructed. In the first paper it was established that two intermediate phases are formed, and in the interval $0.07 < x_{Ge} < 0.55$, the predicted immiscibility. On the contrary, Pani and Palenzona established that Ge and Yb form one congruently melted Yb_5Ge_4 ($T_m = 1640 °C$) and 5 compounds, which melt with decomposition. We believe that various diagrams of the state of the system must be due to different materials purity. To verify which of these state diagrams is correct, we investigated the thermodynamic properties of the melts of the Ge-Yb system by calorimetry at 1340 K in the range of compositions $0 < x_{Yb} < 0.4$ (Fig.).

It is clear that the formation of alloys of Ge with Yb occurs with an exothermic effect. The minimum value of the mixing enthalpy is ≈ -63 kJ / mol (extrapolated from experimental data) at $x_{Yb} \approx 0.45$. This correlates with the phase diagram of the Ge-Yb system constructed by Pani and Palenzona. Another confirmation of the validity of the phase diagram and our thermodynamic data is the melting the Ge-Yb system [Nikolaenko], also established by calorimetry at 1223 K. The results are slightly more exothermic, which can be explained by low temperature of the studies.

Recently a thermodynamic description of the alloys of the Ge-Yb system by the Chalphad method was carried out in [1]. For this the data was used, and also the enthalpies of the formation of ytterbium germanides by the calorimetry method were determined. It was established that $\Delta H_{min} = -68$ kJ / mol, and the formation enthalpies $\Delta_f H$ (Yb_5Ge_3) = -78 kJ / mol. This is all consistent with the fact that the enthalpy of phase formation, usually, is more exothermic than the enthalpy of mixing melts.
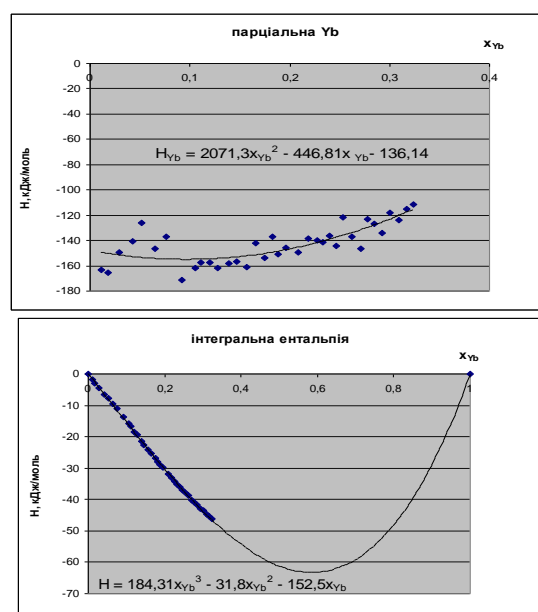
Fig. Partial and integral enthalpies of mixing of melts of the Ge-Yb system

Thus, at present, the thermodynamic properties and phase diagrams of the Ge-Yb system are established reliably and with their participation it is possible to determine the form of the ΔH - dependence and also to use the thermochemical properties of the melts of the Ge-Yb-REM ternary system for predictions if thermochemical properties of the REM- Yb. All this will reduce the volume of experimental studies of both binary and multicomponent systems. This is very important for ytterbium alloys, because this REM has low melting temperature and is highly volatile.

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THE IMPACT OF HIGH VOLTAGE PULSE DISCHARGE BLEND PREPARATION ON THE CEMENTED TITANIUM CARBIDES FUNCTIONAL PROPERTIES

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The use of the Ti and Fe powders mixture blend after high voltage pulse discharge (HVPD) preparation [1] for tungsten free cemented carbides (CC) production makes it possible to eliminate the necessity of expensive and scarce alloying components.

For CC functional properties control it is necessary to provide the possibility of the hard phase and binder ratio changing during blend preparation and its subsequent consolidation.

The solution of this problem is related to the determination of the initial powder mixture composition components ratio and the HVPD variable parameter, as which it is convenient to use the specific energy of the impact W_s. The goal of the work was to determine the values of these parameters.

CC with an iron (steel) binder contain from 40 up to 95 vol. % (30 up to 92 wt. %) of TiC [2], with increasing of its content hardness and wear resistance usually increase, but viscosity and ductility decrease. On this basis, the Ti content (C_{Ti}) in initial mixture with Fe should be from 26 to 90 wt. %.

Experimental studies have made it possible to establish a relationship between W_s and the amount of sintered TiC as a result of the blend HVPD [3], which allows to find the W_s (C_{Ti}) dependence, which can be approximated linearly as $W_s = 0.32 \cdot C_{Ti}$, MJ/kg.

Functional properties control was performed experimentally for CC, the blend for its production have been obtained as a result of the 80 % Ti + 20 % Fe powder mixture HVPD, W_s was 4.5; 9; 18 and 27 MJ/kg.

The prepared blend was consolidated by spark plasma sintering at a holding pressure of ~ 60 MPa, a temperature of ~ 1100 °C for a time of 270 s.

HRA hardness, the loss of mass during abrasive wear on a diamond wheel m_w and the dynamic strength σ_d by Hopkinson-Kolsky method of obtained CC were determined (see Table 1).

Table 1

Properties of the obtained materials

W_s, MJ/kg	C_{TiC}, wt. %	HRA	m_w, kg/km	σ_d, MPa
Initial	0	74.0	4.2	–
4.5	20.5	82.0	3.1	1250
9	34	83.5	3.0	wasn't destroyed
18	61	84.0	1.5	wasn't destroyed
27	83 (+ excess C)	59.5	6	300
VK8 according to the GOST 3882-74	0 (~ 92 % WC)	88.0	8.5	–

Conclusions. The boundary values of the Fe–Ti initial powder mixture composition ratios and the HVPD specific energy were determined, which made it possible to purposefully change the hard phase and binder ratio during blend preparation and its subsequent consolidation and, thereby, control the cemented titanium carbides functional properties.

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MECHANOSYNTHESIS OF CERAMICS COMPOSITE TiC-TiB$_2$.

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Ceramic-matrix composites based on TiC–TiB$_2$ have attracted enormous interest during recent years because, in comparison to single-phase ceramics, they exhibit superior properties including high hardness, good wear resistance and high fracture toughness. The application of TiC–TiB$_2$ composites has been limited due to the fact that they have been difficult to process. Much of the research effort has therefore focused on the synthesis, processing and fabrication of TiC–TiB$_2$ and is based primarily on self-propagating high-temperature synthesis . However, macrocrystalline composite is obtained, which is difficult to process at the next consolidation. Thermodynamic calculations show that boron carbide is unstable in the presence of titanium at low temperatures. Therefore, TiC-TiB2 nanocomposite with a uniform phase distribution can be achieved under milling in a planetary mill.

The aim of this work was to study the peculiarities of formation of phases during milling powder mixture titanium and boron carbide in a planetary mill.

Experimental Procedure.

We used a mixture of titanium and carbon powders in the ratio Ti: B$_4$C = 3: 1 to obtain the TiC - TiB$_2$ composite by the reaction: $3Ti + B_4C = TiC + 2TiB_2$. Milling was carried out under argon atmosphere in a planetary mill AIR-015M, which can reach centrifugal acceleration field 45g in the rotational speed of the carrier 735 rev/min. And roller speed 1840 rev/min. The ratio of steel balls and milled powder was 20:1. X-ray analysis was carried out on the installation DRON3 in copper Cu$K\alpha$-radiation.

The results of the experiment.
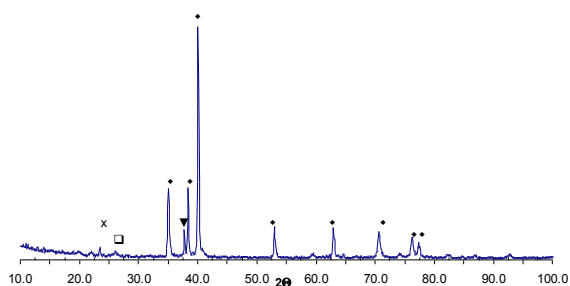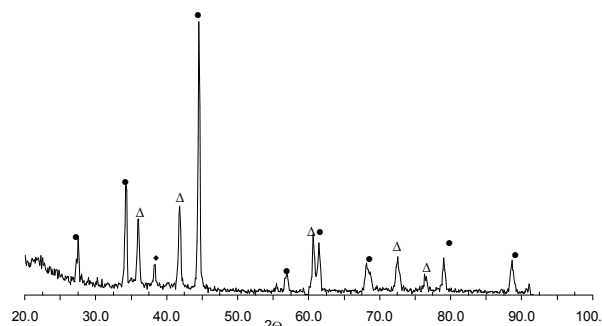
b)
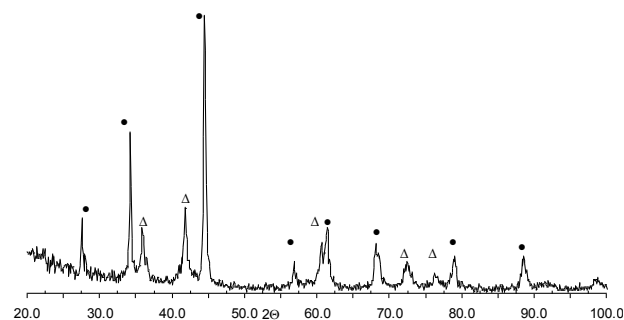
c)

Fig. 1. X-ray diffraction of milled powder mixtures of Ti+B$_4$C after: a – 5 min.; b – 15 min; c – 25min ($\bullet$ – Ti, $\blacktriangledown$ – B$_4$C, x – carbon, $\square$ – B$_2$O$_3$, $\bullet$ – TiB$_2$, Δ – TiC)

The fig.1 shows X-ray diffraction patterns of powders mixture (Ti+B$_4$C) after 5, 15 and 25 min mllling. You can see from the fig.1, b titanium disappears almost completely after 15 min of milling. Only the line of titanium (002) is fixed because its intensity is greatest at this stage of milling. This plane (002) is the lightest sliding plane. The main X-ray lines correspond to the phases TiB$_2$ and TiC.

The mechanism of formation mixtures phases TiB$_2$:TiC (2:1) after milling of titanium and boron carbide is similar to the mechanism of formation of TiB$_2$ and TiC after milling of titanium with boron and carbon and runs by the mechanically-induced reaction of self-propagating synthesis.

a)

THERMODYNAMIC PROPERTIES OF ALLOYS OF Al–Ni–Gd system

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Alloys consisting of Al, Ni or rare-earth metals (REM) are characterized by a number of valuable properties - a tendency to amorphization, reversible absorption of hydrogen, magnetic, and also are strong dispersants and desulphurizers.

Therefore, it is desirable to know their thermodynamic properties for the simulation of the diagrams of the state of these systems and the determination of the optimum conditions for obtaining intermediate phases, alloys and ligatures. Determining them for a liquid alloy is a complicated experimental task due to the high costs of time, materials, and, especially, refractory and aggressive. In this regard, in the first stage, we gathered information on the thermodynamic properties of alloys and phases of the double-limiting subsystems, established the most reliable data, and estimated the similar parameters for the triple Al-Ni-Gd melts on different models. For all models, it has been obtained that the minimum enthalpy of mixing falls on nickel monoaluminide, which melts at high temperature (1923 K). But the process of isenthaphia mixing the melts of the Al-Ni-Gd system differed. To determine which of the models correctly describes the thermodynamic properties of the melts' data, the thermochemical properties of the liquid alloys of this system on the radiant section $x_{Al}/x_{Gd} = 1/1$ at 1700 K. The research was started from an alloy $Gd_{0,5}Al_{0,5}$, which was placed in lined with yttrium oxide. Calibration of the calorimeter was performed by introducing into the liquid alloy of tungsten samples weighing 0.03-0.6 g in the beginning, inside and at the end of the experiment. When adding nickel in an aluminum-gadolinium melt, the sign-thermal heat effects were fixed.

The comparison of the determined enthalpy calorimetry method of the Al-Ni-Gd liquid alloys evaluated according to different models showed that the best agreement is observed with the Redlich-Cister model with a triple input Lo = 200 (figure). This is not surprising, since according to the isothermal section of the state diagram of the system its components form 10 ternary intermetallics, which indicates a strong
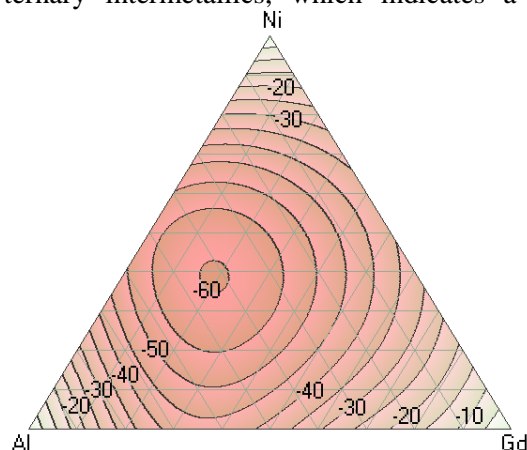
interparticle interaction between different-atom atoms.

Thus, the model used by us for calculations can be used for other Al-Ni-rare-earth metals (REM) systems, which are very little studied, but for which it is very important to have information about the energy of interatomic interaction in a wide range of concentrations.

Figure. Estimated isointalpines of mixing of Al-Ni-Gd melts at 2000 K.

SYNTHESIS OF CARBIDE PHASES IN SURFACE LAYERS OF METALS VIA ELECTRIC SPARK ALLOYING WITH GRAPHITE AND SOME TRANSITION METALS OF IV-VI GROUPS

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The electric spark alloying (ESA) method [1] was applied to synthesize carbide phases in the surface layers of metals using compact electrodes made of graphite, titanium, chromium, molybdenum and tungsten, as well as their powders fed into the inter-electrode gap.

The energy regimes (discharge energy, frequency and duration of electrical pulses) are optimized, at which uniform and continuous layers with the greatest number of carbide phases are formed on the surface of metals.

Fig. 1. Diffractograms obtained from the surface of Ti samples subjected to ESA graphite electrode in different modes (W): a. W = 0,3 J; b. W = 1,0 J

The X-ray phase analysis of the surface layers after the ESA showed the presence of TiC, Cr_3C_2, Mo_2C, WC and W_2C carbides in them, as well as of carbon, titanium, molybdenum, and tungsten in free form. Fig. 1 displays the diffractograms obtained from the surface of titanium samples subjected to the ESA with a graphite electrode. These data confirm the previously obtained results on the example of the ESA of a titanium substrate with a graphite electrode [2].

When the powders of the above materials were used, then multi-phase layers with high physical-mechanical characteristics were formed.

The microhardness of the layers formed by successive treatment with electrodes made of graphite and of any transition metal is comparable to that obtained after the ESA with standard compact electrodes of the type T15K6 or BK8.

Tribological tests of steel and titanium samples with coatings showed a significant (7-10 times) increase in their wear resistance compared to that of uncoated substrates.

It is concluded that the process of the ESA with Ti, Cr, Mo and W graphite and transition metal electrodes is less expensive and may be an alternative to modifying (hardening) the working surfaces of parts with standard electrodes based on tungsten and titanium carbides such as VC and TK.

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TOPICS 3 (C)

Coatings and films based on refractory compounds

THE PROPERTIES OF CR-CO-CU-FE-MN-NI ALLOY AS A FUNCTIONS OF THE DEPOSITION PARAMETERS

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The goal of the investigation to establish the role of discharge current I, energy of ions bombarding growing film E_i, (that is equivalent to the negative bias voltage applied to the substrate, U_b), and condensation surface temperature T_{surf}, in formation of main film properties. High entropy alloy CrCoCuFeMnNi films were deposited by DC magnetron sputtering in Ar at P_{Ar}=3-5 10^{-3} torr.

The film structure was investigated by transmission electron microscopy (TEM) the composition was evaluated using energy dispersive X-ray spectroscopy, condensation surface temperature T_{surf}, was measured by the method described in [1]. The film microhardness was evaluated by means of "Micron-gamma" unit.

Measurements of the surface (T_{surf}) and substrate temperature (T_{sub}) as functions of I and U_b have shown that the T_{surf} grows up faster than that the T_{sub} and their difference reaches the 100–110 K value with increasing both the discharge current I, and the bias voltage U_b.

The composition of films deposited without ion bombardment (U_b=0 V) was similar to that of the sputtering target, see Fig. With increasing the U_b the film composition was gradually depleting in Cu and Mn (Fig).
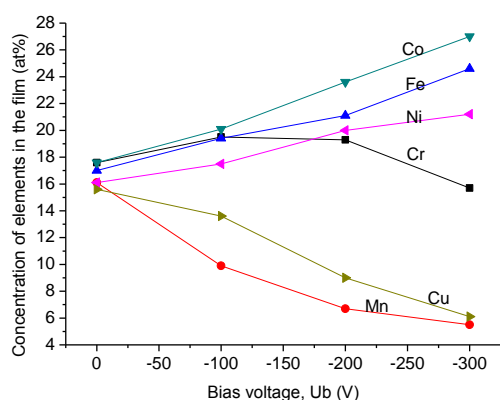
Fig. The concentration of film-forming elements in the films as a function of the bias voltage, U_b.

The possible reason for this effect is the selective re-sputtering of these elements from the condensation surface due to their very weak chemical bonding with other film-forming elements.

XRD-analysis of the structure of sputtering alloy has shown that it consists of two FCC phases with the lattice parameters – a_1=3.61 Å for the main (~76%) phase and the left with a_2=3.68 Å. The electron-diffraction analysis of the films has shown that they also crystallize in two phases. The main phase is also FCC with close lattice parameter a_1=3.73 Å. However, the secondary phase is the BCC one with a_2=3.00 Å which volume is sufficiently smaller. The volume noticeably decreased in films deposited under the IB (U_b =-200 V).The origin of the BCC phase is yet unclear.

Analysis of the film microstructure has shown that the grain size of the FCC phase is larger in average compared to that in the BCC phase. However the increase of the grain size with elevation of the U_b that was character effect for other films wasn't observe in our films. Possible reason is insufficient intensity of the IB (U_b =-200 V) for the films with such composition.

The microhardness measurements have revealed that maximal hardness (H~23 GPa) possessed films deposited at U_b =-100 V. Those deposited at higher U_b =-200 V were lower – H~18 GPa. The reasons for this effect are unclear. Possible reasons are: film densification, changes in its microstructure, intensification of the diffusion processes upon the influence of increased surface temperature T_{surf} under the IB.

Conclusions The most important technological parameter allowing deposition of a film with optimal properties: – composition close to the original, minimal volume of undesirable secondary phase, optimal grain size and density, that provide good mechanical properties of the film, is its ion bombardment with ion energy of around ~100 – 120 eV.

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THE INFLUENCE OF THE DEPOSITION PARAMETERS ON Cr-Co-Cu-Fe-Ni HIGH ENTROPY ALLOY FILMS PROPERTIES

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Basic film properties – composition and structure that define all the other properties of a film strongly depend on the deposition parameters.

The goal of the work presenting is to clarify the influence of: (i) magnetron discharge current I, (ii) negative bias voltage applied to the substrate, U_b, that defines the energy of Ar ions E_i bombarding the growing film, (iii) the condensation surface temperature T_{surf}, on the film composition and structure. High entropy alloy (HEA) films were deposited by DC magnetron sputtering in Ar environment of a target fabricated from CrCoCuFeNi alloy.

The film structure was investigated by TEM, its composition was analyzed using EELS, surface temperature was measured by the method described in [1]. The film microhardness was evaluated by means of "Micron-gamma" unit at a load ≤ 0.05 N.

Measurements of the surface (T_{surf}) and substrate temperature (T_{sub}) as functions of I and U_b have shown that the T_{surf} grows up faster than that the T_{sub} and their difference reaches the 100–120 K value with increasing both the discharge current I, and the bias voltage U_b.

The composition of films deposited without ion bombardment (IB) ($U_b = 0$ V) was equal to that of a target. The effect of depletion of films in copper as the U_b was increasing (Fig) has been revealed earlier for AlCoCrCuFeNiV films [2].
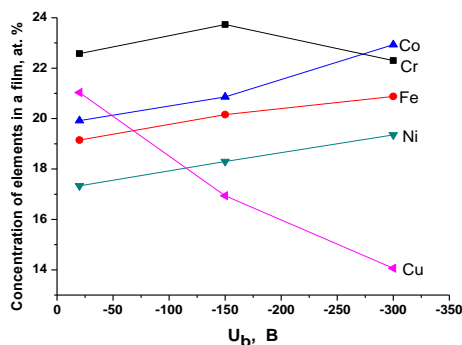
The reason for this effect is the re-sputtering of Cu from the condensation surface as a component which does not chemically bonded with the other alloy components.

XRD analysis of the sputtering target showed that the alloy crystallizes in two phases – FCC (~96%), while the rest phase is BCC. Electron-diffraction analysis revealed that the films deposited without IB possess similar structure. However when the film was deposited under the IB (U_b =-200 V) the BCC phase in such film wasn't revealed.

Investigation of microstructure of films deposited at different discharge currents and bias voltages indicated that the grain size tends to increase with increasing both the I and U_b. The reason for this effect is the increase of the surface temperature T_{surf} due to increasing the energy flux delivering to the growth surface both by sputtered species and bombarding Ar ions.

The microhardness measurements have shown that maximal hardness (~19 ГПа) possessed films deposited under moderate (U_b =-100 V) IB. This effect is a result of several processes occurring in the film under the IB, e.g., due to film densification, changes in its microstructure, intensification of the diffusion processes with increasing the surface temperature under the IB.

In conclusion, it is shown that one can effectively govern basic HEA films properties – composition and structure, by means of such technological parameters that may vary the energy conditions on the condensation surface.

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Fig. The concentration of the alloy elements in a film as a function of the bias voltage U_b.

PREPARATION CARBON NITRIDE FILMS ONTO TITANIUM SUBSTRATE BY THERMAL CONDENSATION OF MELAMINE

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The task of efficiently obtaining of hydrogen as an environmentally clean energy source through photoelectrochemical water splitting is one of the most promising areas of green energy – the energy of the future. Currently, an intensive search of new photoelectrode material for this process is conducted. Titanium dioxide is one of the most common photoanode materials due to cheapness, simplicity in manufacturing, stability in electrolyte photocorrosive solutions and photocatalytic activity in the ultraviolet region, its only drawback is the lack of activity in the visible range of solar radiation [1]. A polymer-like semiconductor, carbon nitride, can act as photoelectrode material for the evolution of hydrogen from water in visible light. In the present experiment thin films of C_3N_4 were deposited on the surface of Ti substrates in two ways: by CVD method and by deposition from an aqueous suspension of pre-synthesized (from melamine) graphitic carbon nitride. Titanium foil 0.5 mm thick and about 0.5 cm^2 was used as the substrate. Powder g-C_3N_4 for the preparation of an aqueous suspension of carbon nitride was synthesized according to the method developed by us earlier [2-4]. The synthesis of films by the CVD method was carried out in the temperature range 500-550°C, melamine was used as a precursor. In the diffractograms of all the samples (Fig. 1a), only two reflexes are present at 2θ = 12.40 (0.714 nm) and 27.49 ° (0.324 nm), which are characteristic for carbon nitride. Due to the low thickness of the g-C_3N_4 coating (submicron according to the scanning electron microscopy (SEM) data (Fig. 1c, d)), the diffraction line at 2θ=27.49°, which characterizes the interplanar distance (0.324 nm) between adjacent nitrogen-carbon planes, is much less intense, than a line of powdered carbon nitride. Due to the low thickness of the g-C_3N_4 films, their IR spectra are more poorly structured. However, in the IR spectra of all three samples (Fig. 1b) there are both an absorption band at 810 cm^{-1} and a series of distinct intense bands in the 1200-1650 cm^{-1} region, which are characteristic for the IR spectrum of graphitic carbon nitride g-C_3N_4.
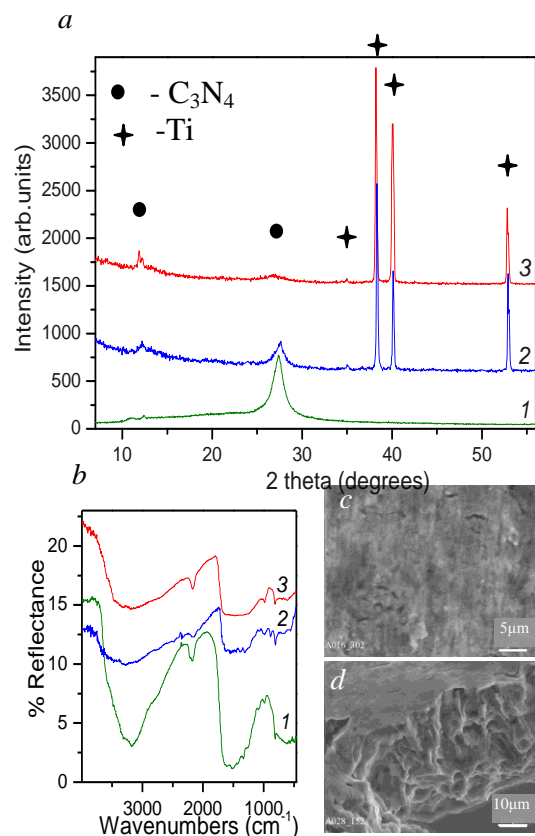
Fig. 1. X-ray diffraction (*a*) and IR spectra (*b*) of: *1* – g-C_3N_4 powder, g-C_3N_4 films obtained: *2* – by CVD method, *3* – by method of deposition from aqueous suspension; SEM images of g-C_3N_4 film obtained by CVD method (*c*) and the edge of g-C_3N_4 film-coated Ti substrate (*d*)

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INFLUENCE OF STRUCTURE ON THE PROPERTIES OF COATINGS OBTAINED BY MULTI-CHAMBER DETONATION SPRAYING

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In modern industry, the urgent task is to increase the reliability and durability of the working surfaces of products operating under conditions of high temperatures and pressures, wear, loads, etc. One of the promising ways to improve the operational properties and durability of products is the application of functional coatings on their surface using a variety of spraying technologies [1 - 2]. The demanded direction of application of the method is spraying of powders of various systems [3 - 4].

The purpose of this paper is to study the structure (phase composition, microhardness, grain and subgrain structure, dislocation density, dispersed micro- and nano-particles, their composition and distribution), and the properties of coatings: Ni-Cr-Si; WC-Co-Cr; Cr_3C_2-NiCr; Cr_3C_2-TaC-NiCr; Al_2O_3-Ti; Al_2O_3-Al; $ZrSiO_4$ sprayed on various substrates materials (steel, copper, aluminium, titanium, etc.)

The structure was studied using a complex of experimental methods of modern materials science, including optical metallography (Versamet-2, Japan; Leco-M400, USA), scanning electron microscopy (Philips SEM-515, Netherlands), X-ray crystallography (DRON-UM1) as well as transmission electron microscopy (JEOL JEM-200CX, Japan).

The executed complex of experimental investigations at all the structural levels allowed carrying out analytical evaluations of the specific (differentiated) contribution of different structural and phase factors and parameters, formed in the investigated coatings, in change of strength characteristics and determining the structural factors cardinal influencing the character and distribution of local inner stresses, which are the potential sources of incipience and propagation of cracks in the investigated structural microregions [5 - 7].

It has been established that the largest contribution, up to 60%, to the integral hardening of the coating material is made by dispersed particles of phase precipitates in the matrix of coatings; up to 20% by subgrain hardening; up to 15% by dislocation hardening with a uniform distribution of dislocation density.

High level of mechanical properties and crack resistance of coatings are provided by the optimal structural-phase composition, fine grain (grain size 10...30 μm) and subgrain (subgrain size 0.2...0.5 μm) structures with uniform distribution of strengthening phases (10...100 nm) and the dislocation density.

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UHTC COATING FOR HEAT, EROSION AND CORROSION PROTECTION OF Si-C/C COMPOSITE

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ZrB_2-based ultra-high temperature ceramics (UHTC) of the ZrB_2-SiC system is of great interest due to its high resistance to high temperature oxidation (HTO). The oxidation of ZrB_2-20vol.%SiC base system leads to silicium dioxide and zirconia formation. Silica forms a thin protection film on the surface. The low thermal stability of silica (up to 1700°C) is the main disadvantage of the base system. The introduction of new components into the base material can make it possible to manage the composition of both outer film and the scale.

The aim of the investigation is to determine the ZrB_2-20vol.%SiC-20vol.%AlN plasma coating on Si-C/C composite HTO mechanism by the research of structural-phase state of both initial coating and the one after its oxidation in the thermal-cyclic regime.

The coatings have been deposited by plasma UPU-3D equipment. High-temperature supersonic oxygen-propane-butane flows of 2000°C in a jet have been used for HTO. The coated sample was subjected to cyclic heating during 15 cycles of 2 min. duration. The total heating time was 30 min. The graphite reinforced with carbon fibers coated with Si-film was used (DLR, Germany) as a substrate. Microstructure and local element analysis of both cross-section and coating surface were studied using REM-106 device and Dron-3M for phase analysis in Cu k_α-radiation.

The coating of 320…370 $\square$m depth was characterized with heterogeneous structure and dense adherence to substrate without pores and cracks. The main phases of initial coating were ZrB_2, AlN and SiC. This corresponds to the composition of sprayed powder mixture. A small amount of ZrC is also formed due to surface coating oxidation and carbon diffusion from substrate at spraying.

ZrO_{2mon} was formed as a main phase in the coating as a result of both HTO and intensive phase formations. Mullite (kianit) Al_2SiO_5 in a small amount and zircon $ZrSiO_4$ were formed as well.

A thin oxide film of some microns depth was formed. Its composition corresponds to mullite solid solution based on silicium dioxide according to the element analysis. Such film having higher resistance to oxygen diffusion must increase the coating resistance to HTO compared with the base system. It is confirmed by positive results of coated samples oxidation. The coating did not exfoliate, cracks and defects on a surface as well as in the coating volume were absent. The oxidation speed was $<7\square$m/min.

Based on experimental data the mechanism of plasma coating HTO in thermal cycling regime (2000°C, 30 min) was proposed. The mechanism is concluded in the scale formation which is consisted of Al_2SiO_5 mullite solid solution strengthened with spheroidized ZrO_{2mon} particles.

HIGH-TEMPERATURE OXIDATION BEHAVIOUR
OF Fe(Ni)CrBSiC-TiB$_2$ COMPOSITE POWDER MATERIALS

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An important characteristic of composite powder materials for gas-thermal spraying of protective coatings is the resistance to high temperature oxidation, which allows us to evaluate the possibility of the coatings operation at high temperatures. The goal of study is to investigate the oxidation behaviour of ПГ-Ж14 (Fe(Ni)CrBSiC) self-fluxing alloy based composite materials with 20 wt.% TiB2 additives at high temperature.

The investigation of oxidation behaviour of Fe(Ni)CrBSiC-20%TiB$_2$ composite powder material at high temperature (up to 800 $^{\circ}$C) was carried out by using the Derivatograph Q -1500-D device. The oxides composition on the composite materials surface was determined by the scanning electron microscope JEOL-9500FS equipped with energy-dispersive spectroscopy (EDS) analyser and the Dron-3 diffractometer for X-ray diffraction analysis.

Composite material of the Fe(Ni)CrBSiC-TiB$_2$ system was produced by sintering in vacuum at 1100 $^{\circ}$C. The chemical interaction between components of self-fluxing alloy and refractory compound occurs during sintering process and results in formation of additional chromium-based boride phases. The structure of composite material of Fe(Ni)CrBSiC-TiB$_2$ system consists of iron-nickel based matrix and grains of titanium diboride and complex chromium-molybdenum-iron boride.

There are two temperate effects on the DTA-curves of Fe(Ni)CrBSiC-TiB$_2$ composite material: the first temperature effect is within the temperature range of 445 - 550 $^{\circ}$C, the second exothermic effect is in the temperature range of 570 - 730 $^{\circ}$C (Fig. 1).
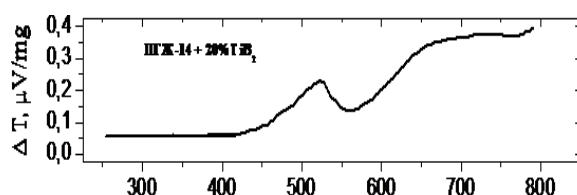
Fig. 1. DTA-analysis of Fe(Ni)CrBSiC-TiB$_2$ composite material oxidation

Fig. 2 shows the structure of composite material surface after oxidation at 500 $^{\circ}$C during 1 hour. According to quantitative EDS and X-ray diffraction analyzes the titanium diboride oxidation occurs at temperatures of 445-550 $^{\circ}$C that results in the formation of titanium and boron oxides:

$$2TiB_2+5O_2=2TiO_2+2B_2O_3$$
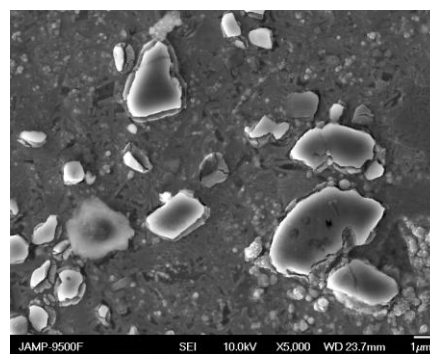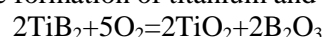
Fig. 2. Structure of Fe(Ni)CrBSiC-TiB$_2$ composite material after oxidation at 500 $^{\circ}$C during 1 hour

The Fe(Ni)CrBSiC-TiB$_2$ composite material oxidation at 700 $^{\circ}$C during 1 hour results in the oxidation of the metal matrix components and the formation of iron and silicon oxides (Fig. 3).
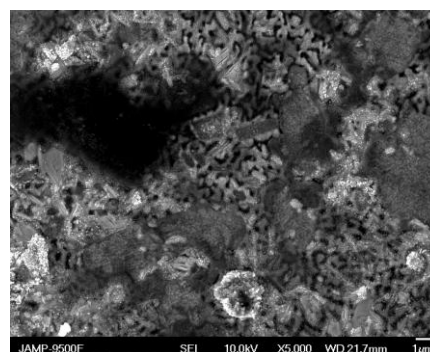
Fig. 3. Structure of Fe(Ni)CrBSiC-TiB$_2$ composite material after oxidation at 700 $^{\circ}$C during 1 hour

DAMAGEABILITY AND FRACTURE RESISTANCE OF THE EDGES OF THE HARD METAL CUTTING TOOLS WITH A MODIFIED WORKING SURFACES

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To ensure performance features of cutting tool different methods of cemented carbide modification are used. Cemented carbide cutting tool modified with PVD coatings is widely used and the method of magnetic-abrasive treatment (MAT) of cutting plates is becoming widespread as polishing and strengthening treatment. As usual limit state for cutting tool is wear, and the effect of these methods of modification on wear-resistance is well known. Analysis of tool refusals in the processing of heavy machines shows that along with the refusal due to wear a significant part of the refusals is caused by the fracture of brittle cutting edge, which shows up in microchipping and chipping.

Regarding this, the brittleness of the coating can be considered as a limiting factor.But there are no results about influence of PVD coatings and MAT on microchipping and chipping.It is extremely important to determinethe effect of the modification of cemented carbideon the parameters of damageability and fracture resistance of the cutting tooledge. The present study is devoted to solution of this problem.

To determine the parameters of damageability and fracture resistanceof the cutting edge a special loading device is developed. As the load element (indenter) carbide or polycrystalline superhard material plate is suggested. We scanned front or back surface and the load values on the indenter were controlled by use of etalons with different weight. Cemented carbide cutting plates PNMM 120408 (WC – 92%, Co – 8%) were tested in original state, modified with PVD - columnar coating TiAlN and after MAT.

As a result of scanning semi-elliptical brittle chips wereformed on the side surface of the plate. The average values ofthe characteristic size of the chip and the ratio of the applied load to this size were considered as a criterion of damageability and fracture resistance.

The use of the statistical analysis of test data on the basis of Weibull distribution allows us to obtain valid values of the guaranteed level of strength characteristics. Along with uni-modal Weibull distributionbi-modal Weibull distribution is used to analyze test data due to the following consideration:a significant deviation from the uni-modal distribution, especially in the area of low strength values. These low strength values are critical for the performance of cutting too and characterize the cases of particular large edge chips.

Modification of the tool material leads to changes in edge mechanical behavior under the local loading. In some range of local loading, the application of brittle columnar wear-resistant coating results in implementation of mechanisms of brittle fracture, increase of mean sizes of chips and reduction of cutting edge fracture resistance.Over the entire range of local loads on the indenter MAT reduces the parameters of cutting edge damageability and increases fracture resistance as compared with the original state of cemented carbide cutting plate.

It is shown that for a reliable prediction of the mechanical behavior of carbide materials under local edge loading the statistical analysis of test data on the basis of multi- modal distribution is necessary.

BIOMINERALIZATION OF WORKING SURFACES OF TRIBOELEMENTS

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Modern technological methods of surface hardening open unlimited possibilities for the creation of protective structures for tribotechnical purposes. The formation of such structures on the working surfaces of machine parts, mechanisms and technological equipment helps to increase their reliability, durability and labor productivity.

A promising trend in the development of new tribotechnical technologies is the synthesis of combined coating methods on the contact surfaces of the working organs of the tribosystem. To improve the process of run-in to the surface of the coatings, thin biofilms are applied. The essence of this technology lies in the fact that biofilms that form on the working surface are the site of interaction of bacteria in the cycles of sulfur, chlorine, phosphorus, i.e. the place of development of biochemical processes. As a result of these processes, biomenealisation occurs, which contributes to the accumulation of biogenic products (elemental sulfur, sulfides, chlorides, fluorides, selenides, alum, etc.) capable of modifying the contact surfaces of the tribosystem [1].

The purpose of the study is the influence of biofilms on the process of coatings' overcoating.

The formation of biofilms on the coatings was studied in two versions: on Postgate medium "B" with ferrous sulphate and on the same medium with sodium sulfate, that is, without Fe (II). Iron sulphide also accumulated in biofilms formed on the surface of these alloys [2].

Microscopic studies of biofilms showed that a small precipitate of sulfides formed.

These observations indicate the role of Fe (II) as an environmental factor that has a significant effect on the structure of the biofilm. In particular, the uniform distribution of sulfate cells of reducing bacteria determines the uniform distribution of sulphides, which play an important role in the modification of the surface of metals that are being studied.

The effect of 3% molybdic acid on biofilms formed by sulfate by reducing bacteria on coatings has been studied in two aspects. The main attention was paid to a search experimental study for the formation of a molybdenum coating on the surface of biofilms. The formation of nanoparticles of Mo compounds on the surface of bacterial cells and in exopolymer substance was studied. It was possible to observe immobilization of Mo as diffusely on bacteria and exopolymer, and in the form of spherical nanoparticles.

Conclusions. Thin biofilms significantly improve the process of run-in. The period of initial wear is reduced, its intensity and frictional forces are insignificant, the setting processes do not develop, and the emerging secondary structures contribute to optimizing the microrelief of the working surfaces for these friction conditions.

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SOME SURFACE PROPERTIES OF SOLID LUBRICANT COATING (MoS2) DUE TO A LOW FREQUENCY IMPACT IN AN INDENTER ENVIRONMENT OF A METAL BODY

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This work discusses the opportunity of applying mechanical vibrations technology to improve quality and the performance of the surface condition of the solid lubricant (MoS2) coating.

Solid lubricant coating properties allow better sliding of the contacting surfaces, a significant reduction in the coefficient of friction and a reduction in the wear of the friction pairs. Using a solid lubricant coating (MoS2), the research results show that reduction of the coefficient of friction to three to nine times, and the wear resistance increases from four to twenty times.In addition, a search for nano-reliefs covering the surface and the powder (MoS2) was carried out

SYNTHESIS AND ANALYSIS OF THE WEAR AND ROUGHNESS

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The frictional behavior of sintered composite materials based on titanium carbide and nickelide forms the basis for the preparation of structural materials products and operating in the high temperature. The effect of the structural state on the changes in the physical and mechanical properties of composite materials on nitrides, carbides and borides of transition metals is analyzed.Complex investigations into the physicomechanical properties and heat resistance of fabricated materials are performed [1].

The wear patterns of the composite materials were analyzed [2] in tribological tests Fig 1.
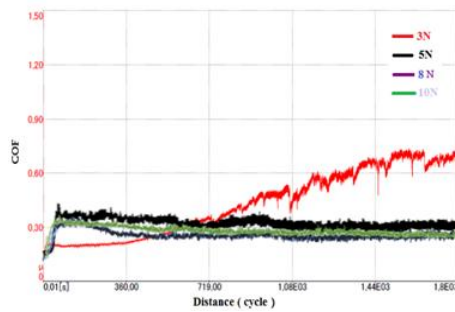
Figure1: Variation in friction coefficient as a function of sliding speed distance and applied load (: 0.35 m / s)

It was also found that the spacing had the greatest effect on the friction coefficient and the wear volume decreased with the increasing of the spacing [3].

The essential differences in the surface topography of samples loaded in dry conditions are confirmed in the analysis of the roughness parameter evolution [4] fig 2. a. The following 2D parameters were considered: In the unloaded state, flattened asperities can be observed on the deformed surface Fig 2.b.

(a)
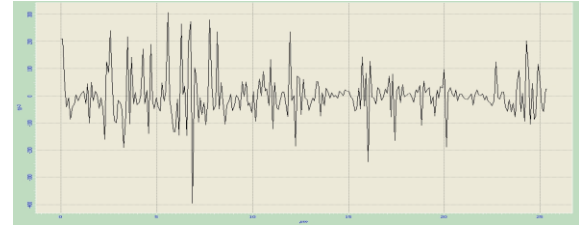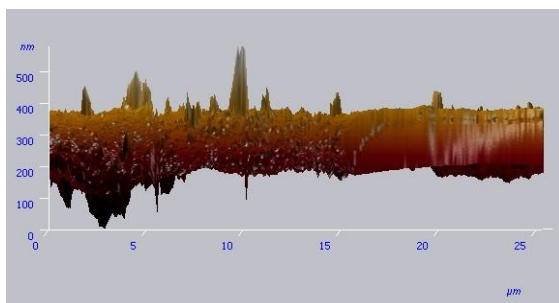
(b)

Figure2: *a)- measurement 2D of surface topography in order to investigate its frictional behaviour. b) Profile corresponding to real area.*

The predicted values were compared with experimental results Table 1.

Table: *Roughness parameters of the deformed surfaces of the samples in figure 1.a*

Max	Min	Ry	Rz
577,339 nm	430,073 nm	147,266 nm	506,714 nm
Average	Ra	Rq	Dispersion
510,674 nm	28,7048 nm	511,831	34,3946 nm
Rsk	Rka	Entropy	Redundancy
-0,157453	-0,696865	7,88768	-0,0936811

The composite materials were shown to significantly enhance the hardness, as well as heat and wear resistances, of the composite materials and are recommended for use in the protection of critical components

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ЭЛЕКТРОДНЫЕ МАТЕРИАЛЫ НА ОСНОВЕ WC, TiC, Mo$_2$C i TiB$_2$ ДЛЯ ФОРМИРОВАНИЯ ЭЛЕКТРОИСКРОВЫХ ПОКРЫТИЙ

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С целью формирования твердых износостойких электроискровых покрытий на металлической подложке были разработаны новые электродные материалы на основе WC, TiC, Mo2C i TiB2.

Было исследовано влияние технологии изготовления электродных материалов на процесс массопереноса и свойства покрытий.

Полученные сплавы имеют мелкодисперсную структуру с размером зерен основной фракции 1-2 мкм, твердостью 26-30 ГПа.

Исследованы структура и функциональные характеристики электроискровых покрытий из разработанных сплавов: твердость 14-24 ГПа, толщина 40-120 мкм.

Окалиностойкость покрытий из разработанных материалов существенно выше по сравнению с покрытиями из сплава Т15К6, а стойкость полученных покрытий при абразивном износе и износе в условиях сухого трения скольжения свидетельствуют о возможности эффективного использования электроискровых покрытий из разработанных электродных материалов для упрочнения быстроизнашивающихся деталей машин и механизмов.

Исследован способ послойного нанесения на металлическую поверхность электроискрового покрытия из металла группы Cu, In, Pb, Cd, Sn и покрытия из Ti, V, W, карбидов или твердых сплавов типа ВК, что позволило существенно повысить качество и износостойкость металлических поверхностей по сравнению с покрытием без подслоя.

Установлено, что спеченные электродные материалы состава (10-30) мас.% сплава (Ni-Cr-Si-B) – ВК6 позволяют формировать электроискровые покрытия толщиной до 100 мкм и микротвердостью 12,3-14,2 ГПа.

Износостойкость и долговечность таких покрытий существенно выше, чем у покрытий, полученных при использовании стандартного твердого сплава ВК6.

Были нанесены покрытия электродом из материала ВК6–10%(Ni,Cr,Si,B).

Такой композитный материал обеспечивает высокую стойкость при газоабразивном износе. Толщина сформированного покрытия составляет 80-100 мкм, а микротвердость 14,0 ГПа.

Практический опыт подтвердил эффективность использования процесса электроискрового поверхностного упрочнения и восстановления изношенных металлических поверхностей деталей машин, технологического оборудования и инструментов.

SYNTHESIS OF CARBIDE PHASES IN SURFACE LAYERS OF METALS VIA ELECTRIC SPARK ALLOYING WITH GRAPHITE AND SOME TRANSITION METALS OF IV-VI GROUPS

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The electric spark alloying (ESA) method [1] was applied to synthesize carbide phases in the surface layers of metals using compact electrodes made of graphite, titanium, chromium, molybdenum and tungsten, as well as their powders fed into the inter-electrode gap.

The energy regimes (discharge energy, frequency and duration of electrical pulses) are optimized, at which uniform and continuous layers with the greatest number of carbide phases are formed on the surface of metals.

The X-ray phase analysis of the surface layers after the ESA showed the presence of TiC, Cr_3C_2, Mo_2C, WC and W_2C carbides in them, as well as of carbon, titanium, molybdenum, and tungsten in free form. Fig. 1 displays the diffractograms obtained from the surface of titanium samples subjected to the ESA with a graphite electrode. These data confirm the previously obtained results on the example of the ESA of a titanium substrate with a graphite electrode [2].

When the powders of the above materials were used, then multi-phase layers with high physical-mechanical characteristics were formed.

The microhardness of the layers formed by successive treatment with electrodes made of graphite and of any transition metal is comparable to that obtained after the ESA with standard compact electrodes of the type T15K6 or BK8.

Tribological tests of steel and titanium samples with coatings showed a significant (7-10 times) increase in their wear resistance compared to that of uncoated substrates.

It is concluded that the process of the ESA with Ti, Cr, Mo and W graphite and transition metal electrodes is less expensive and may be an alternative to modifying (hardening) the working surfaces of parts with standard electrodes based on tungsten and titanium carbides such as VC and TK.

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Fig. 1. Diffractograms obtained from the surface of Ti samples subjected to ESA graphite electrode in different modes (W): a. W = 0,3 J; b. W = 1,0 J

ELECTRODE MATERIALS ON THE BASE OF TITANIUM CARBIDE AND TUNGSTEN CARBIDE FOR ELECTROSPARK COATING

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Scientific researches as well as practical expertise confirm close relationship between erosion characteristics of the electrode materials for electrospark coating of the layers with different purpose and their structure, phase composition, production technology.

For hardening of the worn surfaces of machine and mechanism details the electrode materials on the base of titanium and tungsten carbide with Co, Cr, Ni, Fe, Si, Al binders were developed. These materials were selected because they form heat-resistant and wear-resistant phases during hot pressing of powder mixtures.

In the Table 1 properties of the electrospark coatings on the base of WC–TiC alloys with (Co–Ni–Cr–Al) and (Co–Cr) binders on the steel 45 surface are presented.

Table 1

Electrode material, % (weight)	HV, GPa	I, mg/m	$\Delta P/S$, mg/cm^2 (750°C, 30 h)
WC–TiC–10(Co–Ni–Cr–Al)	21	–	12,0
WC–TiC–20(Co–Ni–Cr–Al)	823	0,16	8,5
WC–TiC–Mo$_2$C–10(Co–Cr)	14,5	0,24	4,0
WC–TiC–Mo$_2$C–10(Co–Cr)	12	0,19	2,0
Steel 45	2,7	0,31	18,0

I, mg/m – intensity of the abrasive wear on the friction way 15 m.

Thickness of the hardened layers (δ) on the steel 45 was 100–120 μm

In the Table 2 properties of the coatings on the base of TiC alloys on the steel 45 surface are presented.

Table 2

Electrode material, % (weight)	HV, GPa	Friction characteristics	
		I,mg/km	f
TiC–5Mo$_2$C–10Co–5Cr	12,0	5,2	0,5
TiC–5Mo$_2$C–10TiN–12Co–5Cr	14,2	3,9	0,56
TiC–12Co–3Ni–0,5C	11,9	1,2	0,65

Abrasive worn out of the formed coatings on the steel 45 on the friction way 15 m was 0,2 mg/m, whereas of the standard TH20 (TiC-Ni-Mo) coatings – 0,31 mg/m. Thickness of the formed coatings was 75–80 μm.

In the Table 3 properties of the coatings made with electrode materials on the base of TiC depending on content of Fe as binder on the steel 45 surface are presented.

Table 3

Electrode material, % (weight)	HV, GPa	δ, μm	$\Delta P/S$, mg/cm^2 (900°C, 35 h)
TiC–20(Fe–Cr–Si–Al)	14,2	120	45,7
TiC–50(Fe–Cr–Si–Al)	11,7	120	34,6
TiC–70(Fe–Cr–Si–Al)	9,5	130	–
TiC–90(Fe–Cr–Si–Al)	8,4	160	30,0
Сталь45	2,7		78,0

Coating test on the steel 45 surface in conditions of abrasive wear has shown that wear-out of the workpieces with coatings made with alloys with 20% and 70% binder content was 0,13 and 0,17 mg/m, respectively, as wear-out of the steel 45 without coating was 0,3 mg/m (friction way 15 m).

The study has shown that protective electrospark coatings of the developed electrode materials on the base of titanium carbide and tungsten carbide on the steel 45 are characterized with high hardness, wear-resistance, and hot-resistance.

INFLUENCES OF DEPOSITION PARAMETERS ON CHARACTERISTICS OF TiN COATINGS PREPARED BY PIII&D TECHNIQUE

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Plasma immersion ion implantation and deposition (PIII&D) method is realized when high-voltage pulse bias potential is applied to the substrate. In this case the coating deposition occurs under conditions of intense ion bombardment, which makes it possible to synthesize the coatings with a dense structure and reduced level of compressive stresses [1, 2]. The aim of this work was to study the influence of the pulse bias potential parameters on the structure and properties of TiN coatings deposited from the filtered vacuum arc plasma with different deposition rates.

Using electron microscopy and X-ray diffraction analysis it was found that variation of negative pulse bias potential amplitude (U) from 0.5 to 2.5 kV, the repetition frequency (f) of pulses from 2.5 to 24 kHz and the pulse duration (τ) from 6 to 20 µs does not cause the major changes in composition and microstructure of coatings.

The only phase in the coatings is TiN nitride with a cubic structure of the NaCl type with an axial-type texture. The coatings have an almost stoichiometric composition (N/Ti ratio of 1±0.1) and a dense columnar microstructure.

The level of compressive stresses and the size of crystallites in coatings vary non-monotonically depending on the parameter $U \cdot f \cdot \tau$ (Figure 1). The maximum stress value 9-10 GPa are observed in coatings deposited under condition the $U \cdot f \cdot \tau$ close to 50-100 V.

It was found that with further growth of $U \cdot f \cdot \tau$ the efficiency of the stress reduction is determined by the coatings deposition growth rate. High deposition growth rate provides a lower level of stress and a larger crystallite size in the coatings. At the same time, the deposition growth rate has practically no effect on the preferential orientation of the TiN crystallites in the coatings. The axis of the texture is determined by the value of the amplitude of the bias potential U. The influence of the parameters of thermal peaks arising as a result of ion bombardment, as well as the processes of sputtering and radiation heating of the deposition surface, on the structure-stress state of coatings is considered.

The method of nanoindentation revealed that all coatings have similar hardnesses in the range of 28-36 GPa and Young's moduli 375-460 GPa.

a

b
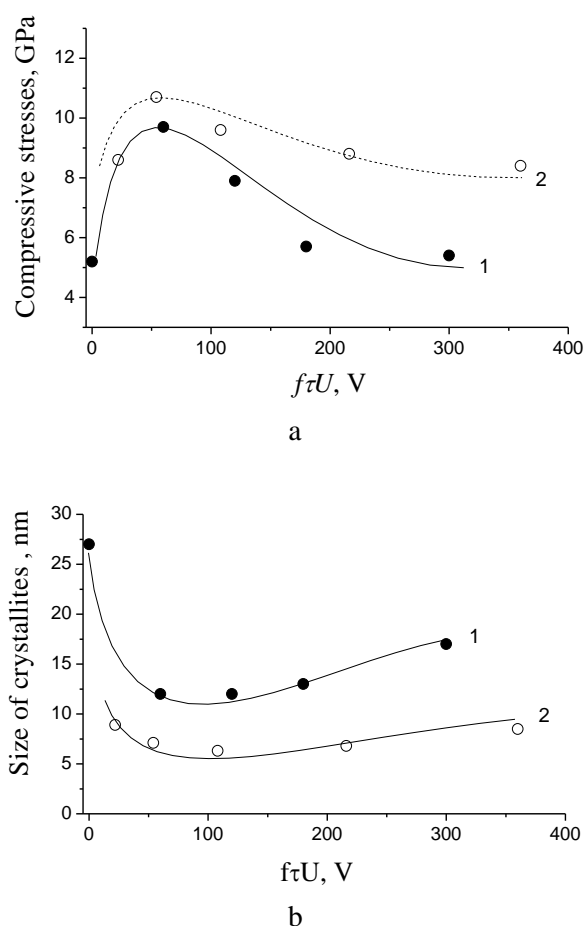
Fig. 1: Stress (a) and size of crystallites (b) in TiN coatings as a function of voltage–frequency- pulse duration value at different values of coating deposition growth rate: 1 – 18 µm/h; 2 - 5 µm/h.

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INTRINSIC STRESSES IN NITRIDE COATINGS DEPOSITED FROM INCLINED ION BEAM IN MODE OF PULSE BIAS POTENTIAL

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The characteristic feature of nitride coatings obtained by the methods of plasma immersion ion implantation is the initiation of the intrinsic stress σ capable to bring about destruction of coatings. Determination of the intrinsic stress value and its dependence on the deposition process parameters and thermal characteristics of coatings is necessary to select the optimum deposition mode and control the quality of the coatings formed.

Formulas for calculating deposition temperature T_0 and intrinsic stress σ in coatings deposited in the pulse potential mode from the beam of differently charged ions obtained within the model of non-local thermoelastic peak (NTP) of low-energy ion [1,2] were generalized to analyze intrinsic stresses σ in TiN (CrN) coatings deposited from inclined beam of Ti^+ (Cr^+) ions [3]. We investigated the dependence of σ on parameter $\tau = ft_p$ in the interval $0 < \tau < 1$, where t_p is the duration and f is the repetition rate of the rectangular pulses of the potential applied to the substrate for fixed value of the amplitude of the pulsed potential U. It is shown that in the case of normal incidence of Ti^+ ions and at potential on the substrate $U = 1.5$ kV, the trend of the calculated curve $\sigma(\tau)$ qualitatively coincides with the experimental data [4] (see Fig. 1). It is shown that the function $\sigma(\tau)$ has the unique maximum σ_m at the point τ_m. Both σ_m and τ_m values decrease with increasing of bias potential U in accordance with the following approximate dependencies: $\tau_m(U) = 0.125/U^{1.5}$; $\sigma_m(U) = 2/U^{1.5} + 10$. Here U is given in kV, and σ_m is in GPa.

It is established that in the range $0.01 < \tau < 0.2$ the stress σ varies nonmonotonically with increasing angle of incidence α. It decreases up to the angles of incidence $\alpha \sim 70^o$ with subsequent growth. This behavior of intrinsic stress is due to different contributions in it of the processes of defect formation, sputtering, and deposition temperature at different angles of ion incidence.

Similar behavior is demonstrated by intrinsic stresses in CrN coatings.
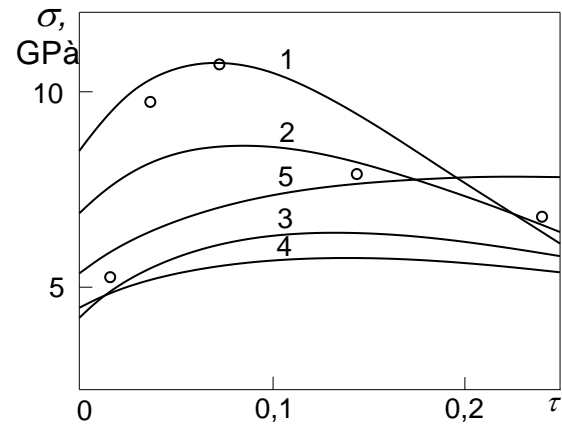
Fig. 2: Intrinsic stresses in the TiN coatings deposited from the Ti^+ ion beam in the pulsed mode at angles of incidence $\alpha = 0^o, 45^o, 60^o, 70^o, 80^o$, curves 1 - 5, respectively, and $U = 1.5$ kV; the symbols ○ are experimental points for $\alpha = 0°$ [4].

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ELECTRODEPOSITION OF TUNGSTEN COATINGS FROM TUNGSTATE-METAPHOSPHATE MELTS AND THEIR PHYSICO-CHEMICAL AND EXPLOITATIVE PROPERTIES

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Tungsten coatings are obtained in the KCl-NaCl-Na_2WO_4-$NaPO_3$ melt with the previously determined ratio $0.02 < [PO_3^-]/[WO_4^{2-}] < 0.18$. At metaphosphate concentrations exceeding $[PO_3^-]/[WO_4^{2-}] = 0.18$, tungsten is deposited with phosphides, and adherent coating is not formed.

Tungsten coatings are obtained in the Na_2WO_4-$NaPO_3$ melt with metaphosphate concentration from 0.5 up to 15.0 mol.%. Above this limit, tungsten codeposits with its bronze, and the deposit growth quickly passes into the dendritic stage.

Continuous tungsten coatings are obtained from halide-oxide electrolyte at $T = 973 \div 1073$ K with cathode current densities up to 25 A/dm^2. Continuous tungsten coatings are obtained from oxide electrolyte at $T = 1023 \div 1123$ K with current densities up to 40 A/dm^2.

The selection of reversive deposition parameters was performed for KCl-NaCl-2.5mol.% Na_2WO_4-0.35mol.%$NaPO_3$ and Na_2WO_4-5mol.% $NaPO_3$ electrolytes. Adherent, continuous, and nonporous coatings are obtained from the electrolytes of these compositions at temperatures 923 and 1173 K with current densities 1-15 and 3-25 A/dm^2, respectively. The crystallites size in the deposit has a minimum depending on the current density, and, above 25 A/dm^2, they are significantly enlarged with a simultaneous increase in roughness. As a result, the deposit is regenerated into dendrites.

The tungsten deposition rate in the current density range investigated is 5-15 μm/h in the halide-oxide electrolytes and 20-45 μm/h in the oxide ones; the current yield of tungsten in the form of coating is up to 60 and 95%, respectively.

Adherent, continuous tungsten coatings on nickel, copper, graphite, tungsten, and molybdenum are obtained from halide-oxide electrolytes. In oxide melts, steel 3, 15X, 45, 40X, 30ХГА, tool steel У7, У10, hard alloy ВК6, ВК20, copper- and nickel-plated titanium are added to these substrates.

As the deposit thickens, it changes from single-phase fine-grained into coarser-grained one. Coarse-grained deposit formation was eliminated by application of the reversive electrolysis mode. The ratio of the duration of the cathode period to the anodic one is from 15 up to 50; the anode period duration is $0.5 \div 3.0$ s; the anode current density is from 20 up to 50 A/dm^2. As a result, relatively smooth coatings up to 0.5 mm thick were obtained at the cathode.

Across the complete coating depth, the microhardness does not change and is 4.5-4.8 GPa. The diffusion zone 5-20 μm deep, detected by X-ray spectral microanalysis of the cross section of the sample, indicates the mutual diffusion of coating and substrate elements and ensures good adhesion of the coating. The continuity of the transition of the coating to the substrate is confirmed by the stereoscanograms of the cleaved samples, on which the deposit columnar structure is also clearly observed.

A comprehensive test for wearing resistance is made for samples of steel 45 with tungsten coating. Counter-body is hardened steel 45. As a result, the wear resistance of steel samples increased by 4.5-5.7 times.

Tests of samples of steel 45 with tungsten coatings for abrasion resistance are carried out with the action of 100 μm electrocorundum fraction with a load 52±0.25 N. Due to the coating, the abrasion resistance increased by 2.5-4.3 times.

MANAGEMENT OF MOLYBDENUM AND TUNGSTEN COATINGS STRUCTURE BY CHANGING THE ATMOSPHERE IN THE ELECTROLYSER

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It is determined that molybdenum and tungsten deposits obtained by tungstate-molybdate melts electrolysis have coarse-crystalline structure. Consequently, even at 100-200 μm thicknesses, deposits become rough. We've attempted to make the deposit grains smaller by introducing carbon dioxide into the atmosphere above the electrolyte.

Replacement of the air by inert (argon) atmosphere practically does not affect the deposit structure and grains size. In both cases, deposits are not textured or has a very weak texture <111>. The only difference was the smoother faces of the vertices of the surface grains under the inert gas atmosphere. This similarity of structures can apparently be explained by the fact that, in the melt being in equilibrium with metallic molybdenum (tungsten), the refractory metal is present in the form of oxygen-containing anions with the highest degree of oxidation, and the solubility of oxygen in tungstate-molybdate melts is low. Therefore, the replacement of air with argon does not introduce new components into the melt and has practically no effect on the current yield.

The introduction of carbon dioxide into the electrolyzer atmosphere significantly affects the structure of molybdenum and tungsten deposits. Their grains become much smaller. Increase in CO_2 partial pressure during electrolysis of Na_2WO_4-Li_2WO_4-$10mol.\%WO_3$ melt at 1023 K leads to degeneration into powdered tungsten deposits and to carbon powders co-deposition at the cathode.

The temperature increase reduces the CO_2 effect and, at 1173 K, solid deposits of molybdenum and tungsten were obtained under an electrolysis atmosphere containing up to 100 vol.%. of CO_2. However, at the same temperature in the Na_2WO_4-WO_3 melt, carbon is deposited at the cathode (up to 1 wt.%) already under an atmosphere containing 25% (v/v) of carbon dioxide. Apparently, this is due to the greater "basicity" of the melt containing sodium tungstate. The oxygen ions activity in it at the same WO_3 concentration is higher than in the Na_2WO_4-Li_2WO_4 melt.

Since, in the ditungstate ion reduction reaction $W_2O_7^{2-} + 12e \rightarrow W + 7O^{2-}$, one O^{2-} ion formed consumes 12/7 electrons, and, in the carbon dioxide reduction reaction $CO_2 + 4e \rightarrow C + 2O^{2-}$, only 2 electrons are consumed, the increase of the activity of O^{2-} ions in the melt causes a less strong displacement of the carbon deposition potential into the negative region than of the tungsten release potential.

This, in turn, favors the deposition of carbon on the cathode. Codeposited carbon acts as a passivating agent, blocking the grains growth of and making the deposit finer. The solid molybdenum (tungsten) deposits retain columnar structure even with 60-70 vol.% of CO2 in electrolyzer). The deposits microhardness increases when carbon dioxide is introduced into the atmosphere.

Apparently, in chloride melts, the passivator is not only carbon, but also the oxygen ion formed during the CO_2 reduction. The latter interacts with refractory metal ions in a melt to form oxycations. Oxycathions are reduced at the cathode to lower oxides, which are included into the cathode deposit along with carbon.

The introduction of CO_2 into the atmosphere above tunstate-molybdate electrolytes changes surface structure and texture of deposits. E.g., at 1123 K (it is especially obvious at 1273 K) with 10÷40 vol.% of CO_2, the deposit grains acquires mainly orientation with <100> axis perpendicular to the substrate surface. Fining of the deposits structure under carbon dioxide atmosphere action allows to obtain molybdenum and tungsten deposits up to 1÷1.5 mm thick.

COMPOSITE COATINGS ON THE BASIS OF DISPERSE-STABILIZED TITANIUM ALUMINIDE

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A promising direction of protection from titanium and its alloys is the development of protective coatings based on γ-TiAl and titanium tri-aluminum are most often used to protect against high-temperature oxidation. However, these coatings in many cases have an insufficient level of tribological characteristics. It is shown that a sharp increase in wear resistance of gas-thermal coatings based on titanium aluminides can be achieved due to the formation of ultrathin inclusions of solid carbides in their structure. Comparative tests of the developed coating with inclusions of TiC and commercial coating containing inclusions of Cr_3C_2 in the NiCr matrix showed the advantage of the former.

The Ti-Al-B system is one of the most promising for the development of protective coatings with improved performance. However, most publications in this area are devoted to the investigation of coatings formed by magnetron sputtering of targets in the form of nanostructured thin films.

Sputtering of gas-thermal coatings from Ti-Al-B powders obtained by mechanical doping can also allow the synthesis of unusual structures with high performance characteristics by forming a material with a disperse-hardened microstructure consisting of an intermetallic matrix with fine inclusions of titanium diboride. In addition to the extremely high hardness (34 GPa), titanium diboride is characterized by high chemical resistance to various aggressive media in a wide range of elevated temperatures. Both indicators, as is known, create the prerequisites for ensuring high friction characteristics and resistance to abrasion. The phase formation of detonation coatings deposited from Ti-Al-B powders was studied. The alloy powders were obtained by mechanical alloying. The use of polyphase nanostructured materials activated by mechanical alloying makes the process of phase formation of gas-thermal coatings sprayed from them more versatile and controllable due to a more active and subtle reaction of the material with the gaseous medium.

It has been found that due to the variation in the composition of the gaseous medium during the detonation-gas spraying process from such an activated powder, it is possible to consolidate composite coatings with different phase composition affecting the properties. The use of argon for purging and transporting the powder into the zone of the combustible gas of the mixture leads to the formation of a coating from the intermetallic matrix from isolated inclusions of titanium borides. When air is used, the phase composition of the coating is supplemented by the inclusion of oxides of titanium and aluminum, oxynitride, which leads to an increase in its hardness. The use of nitrogen leads to the formation of a coating whose microstructure base is a random two-phase mixture of intermetallide and nitride phases TiN, AlN containing inclusions of borides, as well as free aluminum and titanium.

In the future, it is of interest to evaluate the physical and technical characteristics of the developed coatings depending on the parameters of the microstructure. Based on the experience of the behavior of the previously studied Ti-Al coating containing nitrides, it can be expected that the developed coatings with nitride inclusions will be effective for working in friction sliding pairs, especially with structural steel. A more solid composite coating with oxide inclusions seems to be promising for protecting parts from abrasive wear.

PECULIARTIES OF PRODUCING COMPOSITE POWDER MATERIALS AND COATINGS BASED ON TITANIUM DIBORIDE

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Titanium diboride has a high hardness and good resistance to oxidation, it is a promising alternative to the Cr_3C_2 chromium carbide traditionally used in wear-resistant compositions operating at high temperatures. The main methods of synthesis of boride phases of titanium: synthesis from elements (sintering or fusing), carbothermic method, carbide, borotermic, deposition from the gas phase, electrolysis of molten media. The most common methods of synthesizing titanium diboride are sintering or fusing of compacted mixtures of titanium and boron powders. Typically, the synthesis of titanium borides from elements is carried out in a vacuum furnace at high temperatures (of the order of 1100-1200 ° C). To compare the properties of powder materials and coatings, two powders were obtained by the MASVS method (Belarus) and by standard technology (Ukraine). Among the wear-resistant composite powder materials based on titanium diboride, the TiB_2-Fe and TiB_2-NiCr compositions are currently of greatest use. Both compositions are successfully prepared by synthesizing titanium diboride from the elements in the presence of a binder metal (alloy). The possibility of realizing this process is ensured by the high thermal effect of the formation of TiB_2 (320 kJ/mol).

The resulting powder materials are characterized by a homogeneous composite structure with a grain size of titanium diboride from 1 to 6 μm, the size and morphology of the latter substantially dependent on the composition of the reaction mixture. The introduction of a small excess of boron into the reaction mixture (of the order of 5%) ensures the formation of titanium diboride and the possibility of amorphizing the metal bundle during rapid cooling. It is shown that among the most promising methods of applying protective coatings based on titanium diboride are technologies of gas-thermal coatings application: high-speed gas-flame and detonation spraying. An additional advantage of these processes is the possibility of preserving the phase composition and fine-grained (up to nano) structure of the composition. When reaction mixtures with an excess of boron are used above the stoichiometric one, the fraction of the solid phase in the coatings is much higher. The best resistance to friction wear is achieved with boride phase content in the compositions of 40 to 60% by weight. Comparative tests of the obtained detonation coatings on friction sliding without lubrication were carried out. The test speed was 8 m/s, with a load of 2.5 kg and a test distance of 2 km. As a counterbody, steel SHKh-15 was used.
The table presents the test results.

The method of obtaining powder	Specific surface area, m^2/g	Hμ powder, GPa	Powder density, g/sm^3	Hμ coating, GPa	Temp. friction, ^0C	Coefficient friction (coating-contour), f
Belarus	0,41	15-20	5,71	16,8±0,85	49	0,21
Ukraine	0,37	16-18	5,52	21±0,9	60	0,25

Table. Physicomechanical properties of composite powders and coatings

ESTIMATION OF QUALITY OF COVERINGS METALLIZED GRIDING POWDERS SYNTHETIC DIAMOND

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Research of an estimation of quality of coverings metallized grinding powders of synthetic diamond carried out on diamonds of mark DS 20 of grinding 100/80. The grinding powders of diamond metallized by a method of chemical restoration Ni and Cu powders, after the diamond have been covered by the thin powder of aluminum witch size of particle (-40) microns by the method of the rolling at the presence of special binding. The dried up metallized powders samples sintered in the furnace in the air environment at temperature 850 °C.

Automated diagnostic of the morphometric characteristics of powders of diamond carried out on device DiaInspect. OSM. At performance of the present work were diagnosed morphometric characteristics grinding powders AC20 100/80 initial, metallized Ni and Cu, and also metallized by composite covering Ni-Al and Cu-Al [1]. For more full estimation morphometric characteristics of grains diamond in addition calculated uniformity morphometric characteristics, which determined by the system – criterion method [2].

Thickness of a covering *(h)* determined under the formula

$$h = \frac{\rho_a}{6\rho_M} \mu D \varphi,$$

where $\rho_a = 3,52$ g/sm^3 – density of diamond; ρ_M – density of metal coverings (g/sm^3); D – the average size of grains of diamond; μ – a degree of metallization which is determined as the relation of weight of the metal spent for a covering, to weight of an initial powder; $\varphi = 0,7$ – the factor of the form.

Calculation made on the basis of an external specific surface of a metallized powder, having accepted 3D models of a grain in the form of a sphere.

It is established as a result of the accomplished calculation, that metallization increases the sized characteristics of grains metallized grinding powders. Improvement of the form of grains for the account for growthing of the roughness of a surface of grains metallized grinding powders is observed increases their rotundity and, improves symmetry. Simultaneously with it uniformity of powders of diamond increases under these characteristics, is especial for metallized grinding powders with covering Cu-Al.

In sense of geometrical interpretation and information in the applied plan is the new morphometric characteristic A_{lg}, showing a relative share of a light part in the common area of a projection of a grain.

It is established, that from set morphometric characteristics researched grinding powders is most sensitive and the used characteristic to estimated of the metallization the relative share of a light part in the general{common} area of a projection is. It is shown, that metallization results to essential (in 1,5–2 times) to increase this characteristic in comparison with initial grinding powders. Such high degree of sensitivity can serve as substantiation for its use by development of criteria of an estimation of quality of a covering.

Therefore the relative share of a light part in the common area of a projection of a grain can be used for an estimation of quality of metallization grinding powders synthetic diamond, namely by criteria of a degree of metallization and uniformity of thickness of a metallized covering on a surface of grains of a powder.

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ELECTRODEPOSITION OF COATINGS OF TUNGSTEN CARBIDE AND ZIRCONIUM AND TITANIUM DIBORIDES FROM MELTS AND THEIR PHYSICO-CHEMICAL PROPERTIES

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Methods for W_2C, TiB_2, and ZrB_2 coatings deposition by electrolysis of ionic melts have been developed. Based on the regularities of the electrodeposition of tungsten, zirconium, carbon, and boron from melts, on the results of the thermodynamic analysis of the decomposition voltages of the corresponding compounds, on the features of the process of the tungsten carbide coatings deposition, a halide-oxide $NaCl$-LiF-Na_2WO_4-Na_2CO_3 melt was chosen, and, for the titanium and zirconium diborides coatings deposition, a halide $NaCl$-KCl-NaF-$K_2TiF_6(K_2ZrF_6)$-KBF_4 melt was selected.

To study the effect of the electrolysis parameters on the properties and structure of W_2C coatings, the optimal $NaCl$-LiF-5.0wt.%Na_2WO_4-0.4 wt.%Na_2CO_3 melt was chosen. Solid deposits was obtained at 1073-1173 K. The adherent uniform non-porous coatings were obtained with cathode current density (2÷15) A/dm^2 and deposition rate (2÷20) μm/h. The W_2C coatings current yield is up to 40-50%, and their thickness – up to 50 microns.

The coarse crystalline structure of the resulting coatings was made more fine by application of a reversive electrolysis mode. It was possible to increase the carbide coating thickness up to 100 μm. Optimum parameters of the reversive mode are as follows: τ_k = 45 s, τ_a = 1.5 s, i_k = (8÷10) A/dm^2, i_a = (20÷30) A/dm^2.

Electrochemically active particles during TiB_2 electroreduction in the $(K,Na)Cl$-NaF-$TiCl_3$-KBF_4 melt are mixed heteronuclear complexes of titanium and boron formed by the interaction of titanium and boron complexes. The temperature threshold for the titanium diboride high-temperature electrochemical synthesis beginning is 873-973K. Optimal temperatures range for coatings obtaining is 1073÷1193 K with cathode current density (5÷25) A/dm^2.

Based on chronovoltammetric studies results, it is established that, in order to ensure a stable joint discharge of zirconium and boron complexes, it is necessary to maintain the molar ratio [Zr(IV)+ B(III)] in the KCl-$NaCl$ melt : [F⁻] > 1:4 while maintaining the ratio [Zr(IV)]:[B(III)] = 1:2. Studies have shown that the temperature threshold for the synthesis beginning in the studied melt is 923÷943 K, and the optimum temperatures range for coatings obtaining is 1073÷1173 K with cathode current density (5÷20) A/dm^2.

The average number of pores per 100 cm^2 under optimal coating deposition conditions is usually 4÷7 for tungsten carbide and zirconium diboride coatings, and 6÷9 for titanium diboride coatings, which indicates their practical nonporosity.

The microhardness of molybdenum carbide coatings is 18÷19 GPa, of tungsten carbide – 29÷31 GPa, of titanium diboride – 30÷32 GPa, and of zirconium diboride – 31÷32 GPa.

As a result of carbide-molybdenum coatings deposition, the steel samples wearing resistance increased 5-7 fold, of carbide-tungsten carbides – 6-9 fold, of titanium diboride – 8-10 fold, and of zirconium diboride – 8-11 fold. The abrasion resistance of steel 45 samples with molybdenum carbide coatings increased 4-6 fold, with tungsten carbide coatings – 7-8 fold, with titanium diboride coatings – 7-9 fold, and with zirconium diboride costings – 8-10 fold.

Corrosion resistance of steel 3 samples coated with W_2C, TiB_2, and ZrB_2 was tested in 3% sodium chloride solution for 96 h, in concentrated HCl (38 wt.%), H_2SO_4 (95.1 wt.%), and H_3PO_4 (85 wt.%) acids solutions at room temperature for 20 h, and in heated up to 80 °C and diluted to 9.5 wt.% the same acids solutions for 8.5 h. Corrosion resistance of samples increases by 10-3000 times compared with the corrosion resistance of the substrate itself; in some media, the coated samples do not practically corrode.

MOLYBDENUM CARBIDE FILMS OBTAINING BY ELECTROLYSIS AND THEIR STRUCTURE CONTROL

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Molybdenum carbide films are deposited from Na_2WO_4-Li_2MoO_4-Li_2CO_3 molten electrolyte with equal concentrations of lithium molybdate and carbonate (within 2.5 mol.%). At the same time, their concentrations should not exceed 20-25 mol.%.

Solid films of molybdenum carbide are obtained at 1073-1223 K and current densities up to 0.5 A/cm^2. At temperatures below 1073 K and current densities above 0.5 A/cm^2, highly disperse molybdenum carbide powders with specific surface area up to 30 m^2/g are obtained. Uniform continuous nonporous films are obtained from Na_2WO_4-5mol.%MoO_3-10mol.%Li_2CO_3 electrolyte at 1173 K and current density 0.01÷0.10 A/cm^2. The films deposition rate within the current density range studied is 5-25 μm/h, and the current yield of molybdenum carbide as a solid deposit is up to 80%. The maximum thickness of the films is up to 100 μm. With temperature increase from 800 up to 950 °C, the average grain size of the crystals is increased from 11.3 up to 17.8 μm at the same cathode current density 0.075 A/cm^2.

Electrodeposition of molybdenum carbide leads to the carbide epitaxial deposition onto the substrate. One way to reduce the grain size is to apply current pulses at the electrolysis beginning or to deposit them in the reversive mode. The cathode density of direct current in all the experiments was $7.5 \cdot 10^{-2}$ A/cm^2. When the electrolysis starts from the cathode pulse, the deposit grains become smaller. For example, at a pulse amplitude 30 A/cm^2 and its duration 40-50 ms, their size varies from 10-14 μm to 3-5 μm. By reducing the grains size, an insignificant microhardness increase of the deposit from 18.2 to 19.5 GPa can be apparently explained.

X-ray studies have shown that initial pulses up to 30 A/cm^2 do not affect the deposit orientation. Regardless of the initial pulse, the molybdenum carbide deposit has the structure (110). When current pulses up to 30 A/cm^2 are applied during electrolysis, only the layers defectiveness increases due to new metal nuclei appearance on each deposit grain. When current pulses with amplitude more than 50 A/cm^2 are applied, the deposit degenerates into spongy and weakly adherent to the substrate one. Apparently, this is typical for conditions of almost complete dimolybdate and carbonate ions depletion of the cathode layer of the electrolyte. The deposit type can be explained by the secondary reduction of $Mo_2O_7^{2-}$ and CO_3^{2-} ions by sodium atoms deposited at the cathode according to the primary reaction and diffusing out of it.

The electrolysis reversive mode application allowed to made coarse crystalline structure finer and to increase the coating thickness up to 200 μm. The optimal parameters are the following: the ratio τ_k/τ_a = 20÷40, the duration of the anode period – 0.5÷2.0 s, and its current density – 0.15÷0.50 A/cm^2.

The current density change from 0.005 A/cm^2 up to 0.10 A/cm^2 does not lead to change of not only the phase composition of the product obtained, but also of the electrocrystallization character during initial time intervals. With further increase of the current density, along with the growth of the Mo_2C layers, lithium oxide is formed. When Li_2O solubility limit is reached in the near-electrode layer, the surface of the carbide deposit is passivated due to lithium oxide blocking. This leads to destabilization of the flat front and to the formation of carbide deposit in the powder form. This is especially the case with the synthesis temperature decrease. Thus, the electrodeposition temperature regime is the most important parameter for the crystallization of molybdenum carbide as a solid deposit.

REGULATION OF PROPERTIES OF SUPERHARD MATERIALS WITH GLASS-COATINGS

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Recently the coatings that are applied to various materials are becoming increasingly important. Wide spread occurrence in practice, coatings formed from silicate melts. They are simple to implement and do not require complex equipment. The coatings act as a transition layer between the grains of the abrasive and the binder and increase of the strength of the abrasive powder fixation in the matrix of the tool. The glass cover applied to diamond powders and cubic nitride boron (cBN) should not only condition high wear resistance of the tool from superhard materials (SHM), but also provide an improved quality of the treated surface, higher productivity when grinding of viscous materials, such as iron-carbon alloys, or hard alloy together with steel.

The most effective in making of glass coverings for SHM powders are the glasses with different transformation temperatures. Their melts had of high wettability and adhesion to abrasive grains. In relation to the diamond, the smallest wetting angle and the greatest work of adhesion has the glass in the system Na_2O–CaO–B_2O_3–SiO_2, and for cBN-glass in the system PbO–ZnO–B_2O_3–SiO_2. In order to increase of the mechanical strength in glassy coatings and materials the dispersed particles are introduced, which inhibit the formation and growth of microcracks. The most promising fillers are the refractory oxides like as Al_2O_3, TiO_2, ZrO_2.

To test this assumption, the aggregates from diamond powders or cBNs with separate glasses in Na_2O–CaO–B_2O_3–SiO_2 and PbO–ZnO–B_2O_3–SiO_2 systems and with a mixture of glasses with the addition of refractory oxides Al_2O_3, TiO_2, ZrO_2 were made. Powders of SHM with glass cover have the form of aggregates consisting of 5–20 grains of SHM, coated and interconnected of glass. A good wetting of refractory oxides Al_2O_3, TiO_2, ZrO_2 (θ <90 deg) by the melting of glasses in the formation of aggregates leads to uniform distribution of their particles in the glass matrix.

The most responsible operation in glass covering is heat treatment, during of all physical and chemical processes are completed providing of making aggregates with optimal physical and mechanical characteristics. The criterion for choosing the temperature of application of glass coverings was the strength index of aggregates (strength of the load on the grain).

When forming coatings on diamond powders with a glass of Na_2O–CaO–B_2O_3–SiO_2 system, and on cBN powders with glass of PbO–ZnO–B_2O_3–SiO_2 system, the optimum temperature is 780–800 °C, which is evidenced by the highest aggregate strength. The combination of a mixture of glasses with different transformation temperatures in these oxide systems allowed, when applying glass coverings on SHM powders, to reduce the temperature of heat treatment on 150–250 °C, depending on the type of abrasive. This is very important for reducing the energy intensity of thermal treatment and for improving the physical and mechanical properties of glass coverings. In mixtures of two or more softened glasses there are diffusion fluxes of ions, directed from the interphase boundary into the particles of glass. Diffusion is a physico-chemical property of glass, the regulation of which makes it possible to regulate the physical and mechanical properties of instrumental composites. Due to the use of a mixture of glasses of different chemical composition, the strength of aggregates of diamonds and cBN is 1.5 times higher than those formed from pure glass.

The introduction in such glass cover as fillers of the refractory oxides (Al_2O_3, TiO_2, ZrO_2) which do not form glasses, but when dissolved in glasses do not weaken, but strengthen glass-like net, allowed to increase the strength of aggregates in 2,8–3 times compared with aggregates from a mixture of glasses without additives. The regulation of the diffusion of multicomponent glasses in such systems can also regulate the properties of the abrasive layer of the tool (for example, the strength, the holding of SHM grains in the binder, wear resistance).

That provides of new properties of the tool, made on the base of the composite material.

THE ROLE OF INTERFERENCE IN ENHANCING MAGNETOOPTICAL EFFECTS IN THIN-FILM STRUCTURES Fe, Co, Ni / REM OXIDE

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Refractory rare earth oxides (REM) are widely used in nanotechnologies. Recently, it was shown that in thin-film structures consisting of contact layers of metals of the iron group (Fe, Co, Ni) and REM oxides, the exchange f-d interaction is carried out between the incomplete f- and d-shells of the atoms forming these layers [1]. The exchange interaction affects the ordering of the magnetic structure of metal layers, which may cause an increase in their magnetization. In turn, the growth of magnetization leads to an increase in magnetooptical effects dependent on it. Since the interference is strongly influenced by the propagation of light in multilayered structures, it is interesting to determine it's role in enhancing magneto-optical effects in structures (Fe, Co, Ni) /REM oxide.

As an let us an example, consider the structure of Fe/Tb_2O_3.
In the presented figure, the dependence of the transmission coefficients T, the reflection of R and the absorption A on the thickness h of the Tb_2O_3 layer of this structure in the case of thin 30 nm (*1*) and a thick 120 nm (*2*) layer of Fe is shown. The wavelength of light is 620 nm.
As can be seen from the figure, the curves T (*h*), R (*h*), A (*h*) mainly have significant extremums, which testify to the strong influence of interference on the passage, reflection and absorption of light in this film structure. And only on the curve (*2*) of T (*h*) dependence at large 120 nm thickness of iron layer are absent, which indicates a decrease in the influence of interference in these conditions. From here we can draw the following conclusion.

In the passing light through a structure in which magnetooptical phenomena such as the Faraday effect are observed, it should be expected that it's enhancement due to f-d interaction of the layers will take place without interfering by use of thick (120 nm) layers of Fe, Co, Ni.
At the same time, in the reflected light, where the Kerr effect is usually observed, the extremums on the curves R (*h*), i.e., the effect of interference, do not disappear even at a large thickness of the Fe layer.
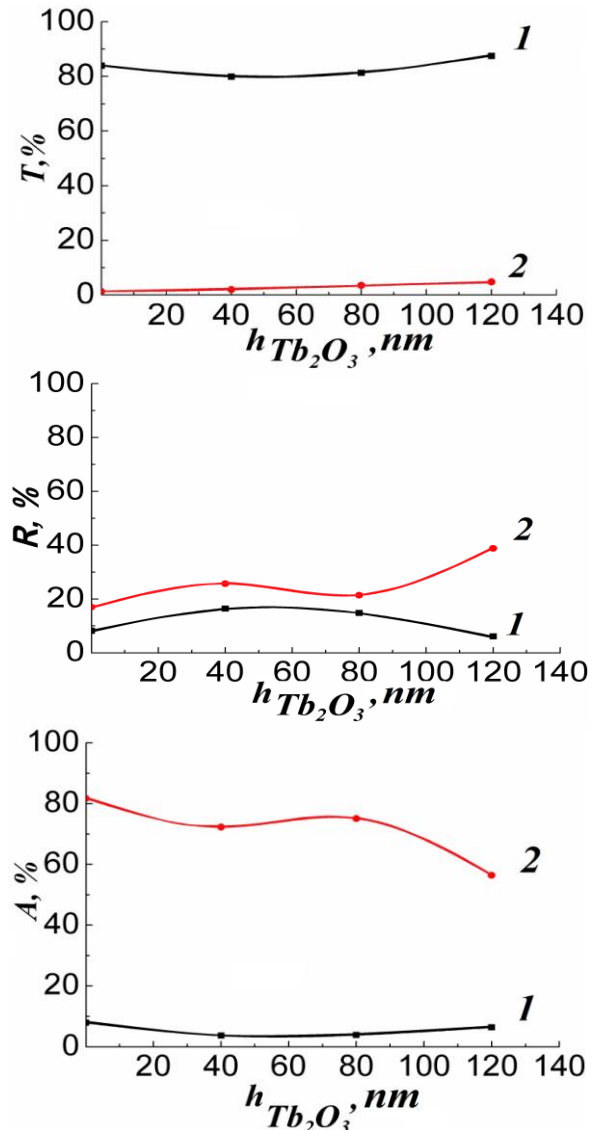
That is, the effect of interference on the Kerr effect enhancement due to f-d interaction in structures (Fe, Co, Ni)/REM oxide remains significant for all considered thicknesses of metal layers. These experimental conclusions are confirmed theoretically.

[1] A.M. Kasumov, V.M. Karavaeva K.O. Shapoval, M.A. Perepelitsa, G.V. Lashkarov, Spectral dependence of the Faraday effect in nanosize Tb_2O_3/Fe structure.1th European Conf. Innovations in Technical and Natural Sciences, Viena – Prague, October 20, 2017, P.127-129.

HIGH TEMPERATURE OXIDATION OF NiSi AND NiSi$_2$ THIN FILMS

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Silicides of transition metals are widely used in the modern silicon film industry because they have metallic conductivity, high melting temperatures, high corrosion resistance, and oxidizability. Schottky diodes, ohmic contacts to shallow-lying active elements, inter-element junctions, gate electrodes in metal–oxide–semiconductor structures constitute by no means a complete list of silicide applications in the very-large-scale integrated circuit (VLSI) technology. Highly conductive nickel silicides are very promising: their conductivity is an order of magnitude higher that of polisilicon and their properties remain stable to temperatures of about 1070 K

In this work the phase formation and thermal oxidation stability of NiSi and NiSi$_2$ thin films on n-type Si (111) substrates have been investigated. The objects to study were thin-film layers of Ni (200nm) on monocrystalline Si substrate of orientation (111) doped with phosphorus. Thin-film system Ni/Si obtained by electron-beam deposition in vacuum 2×10^{-4} Pa. After deposition the samples were annealed in a furnace with oil-free vacuum pumping 1.33×10-3 Pa in the temperature range 470 – 1270 K

For phase identification was performed in "Electronograph EMR-100" using reflection diffraction method. The thermogravimetric analysis (TGA) was carried out in "Derivatograph Q-1500D" thermoanalytical instrument. The sample mass of 20mg was heated in a platinum crucible in static air atmosphere at a rate 5 K/min and a maximum temperature of 1270 K.

The electron-diffraction patterns (circular reflections) indicate that films have a polycrystalline structure (Fig.1). In initial state, the Ni(200 nm)/Si(111) thin-film system has a nickel phase (FCC - lattice, Fig. 1,a). The annealing at 970 K, gives rise to a NiSi phase of orthorhombic structure (Fig. 1,b), no nickel phase residue being observed. This means that silicides from throughout the entire volume of the metal film. The NiSi$_2$ that forms at a higher annealing temperatures (1270 K) has cubic structure (Fig. 1,c). These results are in good agreement with the mass-spectrometric and resistometric data.
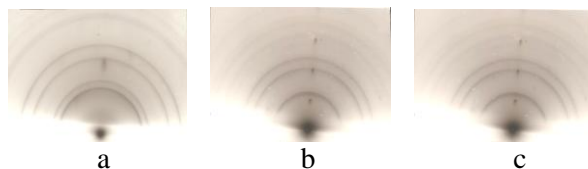
Fig. 1 Electron diffraction patterns of the Ni(200 nm)/Si(111) thin-film system: in the initial state (a) and after annealing in vacuum at 970 K (b) and 1270 K (c).

Such correlation in the Ni(200 nm)/Si(111) reflects the following features of the crystalline interaction between metal and silicon: metal is the predominant diffusing component at low annealing temperature (970 K), whale at high annealing temperature (1270 K), it is silicon that diffuses from the surface layers of the silicon substrate into the film.

According to data TGA (Fig.2), high-temperature oxidation of the NiSi films and the associated increase in weight begins at about 250 degree higher than the oxidation of a silicon substrate. The oxidation of NiSi film starts at 930 K, which is approximately 100 K below the temperature at which NISi$_2$ films start oxidizing.
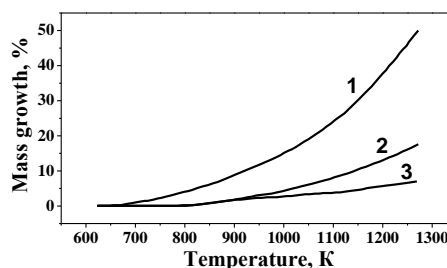
Fig.2 TGA curves of high-temperature oxidation of silicon substrate (1), NiSi (2) and NISi$_2$ (3) films

For both NiSi and NISi$_2$ oxidation types the SiO$_2$ thin protective layers have been formed. When temperature increases, the mass increment NiSi films becomes greater than that of NiSi$_2$ films. This difference is three times as great at 1270 K, which is due to the difference in their structure and stoichiometry. Due to high silicon content, nickel dicsilicide forms dense layers of silica on the surface during oxidation, which has substantial impact on the oxidation rate.

STRUCTURE AND PHASE COMPOSITION OF OXIDE SCALE OF $Nb_{36}Cr_{16}Al_{16}Ti_{16}Zr_{16}$ ALLOY AFTER OXIDATION at 1000 °C

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Nb alloys are promising materials for high temperature applications in the aerospace industry due to the combination of its high mechanical characteristics and high melting temperatures. However, their low oxidation resistance is a significant disadvantage. For increase the oxidation resistance of Nb alloys, a promising direction is creation of multi-component alloys containing an elevated amount of Ti, Al, Si and Cr. However, this in turn contributes to the formation a large number of brittle inermetallic phases, which sharply reduced a physical and mechanical properties of alloys.

Therefore, one of the possible solutions to this difficult problem is the creation of materials of a new generation - so-called high entropy alloys (HEA), the concept of which was proposed by Yeh [1].

The study of the oxidation resistance of the multicomponent $Nb_{36}Cr_{16}Al_{16}Ti_{16}Zr_{16}$ alloy during high temperature oxidation was conducted in this work.

The alloy was obtained by the method of argon-arc melting with a non-consumable electrode. Investigation of oxidation resistance was carried out in an electric furnace in a medium of still air at a temperature of 1000 $^{\circ}$C during 10 hours. The phase composition of the alloy in the initial state and after annealing was investigated by the RFA method on a Dron-3M diffractometer in $Cu_{k\alpha}$ radiation. The data was processed using PowderCell 2.4 program.

In the cast state, the $Nb_{36}Cr_{16}Al_{16}Ti_{16}Zr_{16}$ alloy have two phases: a bcc solid solution and an Laves phase based on $ZrCr_2$ (C14) with a hexagonal crystalline lattice. On the surface of the alloy after oxidation at 1000°C for the 5 h a thin scale of brownish-rust color is formed. Further annealing make for formation of a loose porous scale, which is partially spallation (Fig. 1).°
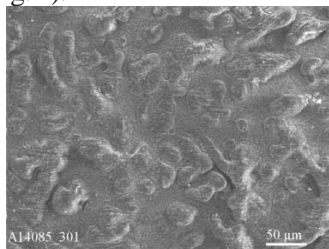
Fig.1 - The morphology of the scale of alloys after oxidation at a temperature of 1000 ° C for 6 hours

X-ray phase analysis was revealed that complex multi phase scale (Table 1) is formed on the alloy surface, which contains $Nb_2Zr_6O_{17}$ oxide with orthorhombic crystalline lattice (*Ima2*) formed by the reaction between Nb_2O5 and ZrO_2 [2] and a rutile type oxide $Ti_{0,952}Nb_{0,048}O_2$, having a tetragonal crystal lattice (P42 / mnm) and the general formula $Ti_{1-x}Nb_xO2$ [3]. Since Ti and Cr are soluble in Nb_2O_5 and form their own oxides with the structure of rutile (α-TiO_2, α-CrO_2) with close lattice parameters [4] and with the possibility of their mutual dissolution, therefore, in this alloy, in addition to $Ti_{0,952}Nb_{0,048}O_2$, is also present another complex routine oxide $Cr_{0,5}Nb_{0,5}O_2$ (P42/mnm).

Table 1 - Phase composition of scale, type of structure and lattice parameters of the corresponding phases after oxidation of the alloy at a temperature of 1000 ° C for 10 hours

Phase composition	Structure type	Lattice parameters, nm		
		a	*b*	*c*
$Nb_2Zr_6O_{17}$	*Ima2*	4,0796	0,4998	0,5310
$Ti_{0,952}Nb_{0,048}O_2$	*P42/mnm*	0,46336		0,3006
$Cr_{0,5}Nb_{0,5}O_2$	*P42/mnm*	0,4497		0,3010

Comparison of the values of the change in the specific mass of samples of the studied alloy with the value for non-alloyed niobium during oxidation for 2 hours at a temperature of 1000 C showed (Table 2) that the alloy $Nb_{36}Cr_{16}Al_{16}Ti_{16}Zr_{16}$ has in a 26 times higher resistance to high-temperature oxidation, which indicates its significantly higher heat resistance.°

Table 2 - Specific mass gain of non-alloyed Nb and alloy $Nb_{36}Cr_{16}Al_{16}Ti_{16}Zr_{16}$

Alloy	q, mg/cm^2
Nb	300
$Nb_{36}Cr_{16}Al_{16}Ti_{16}Zr_{16}$	11,46

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STRUCTURE AND PHASE COMPOSITION OF SCALE ON THE ALLOY Fe$_{30}$Ni$_{25}$Co$_{15}$Cr$_{20}$Al$_{10}$ DURING OXIDATION AT900°C

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A new class of materials with low free energy and high entropy of mixing, so-called high – entropy alloys [1] is widely explore now. Such interest is caused to them by presence of increased operational specifications in wide temperature interval [2, 3]. The aim of this work is research of phase transformations of high – entropy alloy Fe$_{30}$Ni$_{25}$Co$_{15}$Cr$_{20}$Al$_{10}$ during long high-temperature oxidation, as phase composition of such alloys plays a significant role for their future application, and information about change of phase composition at elevated temperature allows to optimise hereinafter operation modes of products on their base.

The high – entropy alloy Fe$_{30}$Ni$_{25}$Co$_{15}$Cr$_{20}$Al$_{10}$of the system is obtained by the method of argon-arc melting with a non-consumable electrode. Research to resistance to oxidation was carried out in electric furnace of the resistance in environment in air at temperature 900 °C with and endurance up to 50 hours. The phase composition of the alloy was investigated on a diffractometer DRON UM-1 in monochromatic Cu$_{K\alpha}$ radiation. The data processing of the diffractometer experiment was carried out using the PowderCell 2.4 program.   In initial state the alloy Fe$_{30}$Ni$_{25}$Co$_{15}$Cr$_{20}$Al$_{10}$ has a dendritic structure (Fig. 1 a). According to the XRD analysis, the alloy contains two solid solutions based on the FCC and BCC structures with lattice parameters a=0,3603 nm and a=0,2862nm, respectively (Fig. 2a).
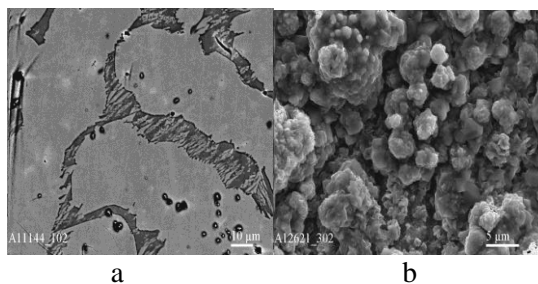
Figure 1 - Microstructure of the alloy in the initial state (a) and the scale morphology after oxidation at 900 ° C , 50 h (b)

After oxidation at 900 ° C for 50 hours, a thin, continuous scaleis formed on the surface of the alloy,without visible chips and cracks(Fig. 1 b), has high protective properties, according to data of X-ray diffraction analysis it is due to formation of difficult multiphase scale, which contains chromium oxide Cr$_2$O$_3$ and spinel NiCr$_2$O$_4$. Since the thickness of the scale is thin and is only 3-5 microns, the reflection from the FCC matrix phase is also observed(Fig. 2, b).
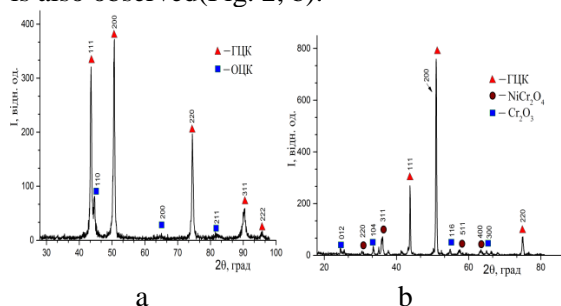
Figure 2 - The diffractograms of the alloy in the initial state (a) and after annealing at 900°C , 50 h (b)

Thus, the high – entropy alloy has high characteristics of heat resistance and is a promising structural material for high-temperature applications.

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ELECTROPHYSICAL PROPERTIES OF THICK-FILM HEATING ELEMENTS BASED ON REFRACTORY COMPOUNDS

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The process of manufacturing thick-film heating elements based on the screen printing of composite materials in the form ofpastes to a ceramic or metal substrate with a dielectric coating, followed by heat treatment of the layers obtained at temperatures of 650-850 ° C. In general, the technology consists of a series of identical cyclespasteapplication. As a resulton the substrate is obtained a set of vacuum-dense alternating dielectric and conductive films. The schematic arrangement of the layers is given in Figure 1 [1].
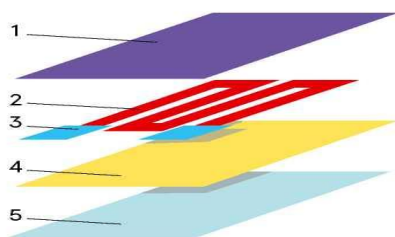
Figure

1.Layout of the layers in the heating element.
1. Protective dielectric layer based on alumino-silicate oxides ($Al-Si_xO_y$). The resistance of the insulation layer is not less than 50 megaohm, with a thickness of 150 μm.
2. The film path from the resistive paste based on nickel-chromium borides ($Ni-Cr_xB_y$), the specific surface resistance of the film is 0.05-50 ohm / cm2, the temperature coefficient of resistance (TCR) is positive.
3. Contact paste based on nickel boride, the specific surface resistance of the film is 0.01-0.05 ohm / cm^2, the adhesion strength with the substrate is not less than 50 kg / cm^2.
4. Dielectric layer based on alumino-silicate oxides ($Al-Si_xO_y$).

The resistance of the insulation layer is not less than 50 MOhm, with a thickness of 150 μm breakdown voltage is not less than 1250V.
5. Ceramic substrate type VK-94, VK-96 or metal substrate type AISI 430, AISI 408, 04X17, 08X17, 15X25T.

The use of refractory compounds, in particular nickel and chromium borides ($Ni-Cr_xB_y$) [2], as a conductive phase of resistive compositions, made it possible to create thick-film heating elements with a wide range of electrophysical and operational properties:
- for supply voltages from 1.5 V to 720 V and the specific surface resistivity of resistive films is from 0.02 to 50 Ohm / cm2;
-the electrical strength of dielectric layers is not less than 1250 V;
- the specific maximum dissipation power can reach 50 W / cm2, and the maximum working temperature is 650 ° C;

The developed thick-film heating elements are successfully used in convectors and air heaters for domestic and industrial use, in factories, reinforced concrete products, industrial steam generators, catering systems and many others, energy savings are achieved through the construction of products and the specific structure of heating elements.

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THICK FILMS ON THE BASE OF
GRAPHENE NANOPLATELETS AND GLASS

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Unique properties of graphene – quasi-two-dimensional (2D) material have predetermined its application in various devices – high-frequency transistors, solar batteries, sensors, catalysts, supercapacitors. However the question of graphene application as a conducting phase when producing films on thick-film technology representing drawing on a substrate of a composite on the base of conducting phase and glass by screen-printing method, remains a little investigated and, accordingly, properties of such films practically are not studied.

So the aim of the work is to investigate the possibility of using of graphene as conducting phase when producing thick films and to study their structure as well as electro-physical properties.

To obtain paste the next components were used: graphene nanoplatelets ("Grafen Chemical Industries Co.", Ankara, Turkey) having the following characteristics:

Diameter (optional), μm	5, 10, 44
Oxygen content, %	1
Purity, %	96-99
Surface area, m^2/g	13-15
Thickness, nm	50-100,

and STs3-55 borosilicate glass and organic vehicle (3 % solvent of ethylcellulose in α-terpineol). The substrate – VK94-1 alumina ceramics with previously formed contact pads of Ag-containing paste ("ESL", USA). Graphene contain in the paste – 1, 3, 5, 10, 15 wt. %. Thick films were screen printed onto the substrate followed by drying (T = 100 ^{o}C, on air) and heat treatment in shaft vacuum electric furnace SShVZ-1.2,5/25-I3 type (vacuum level – 10^{-5} atm) at the temperature of 800 ^{o}C during 10 min. Film thickness – ~200 μm. Film structure was studied with scanning electron microscope JEOL JSM-6490(LV) supplied with EDS local microanalyzer. Volt-ampere diagrams, temperature dependences of electrical resistivity were also investigated and temperature coefficient of resistivity (TCR) was determined.

Insertion of 1 to 3 wt. % of graphene is shown not to result in emerging of composite electroconductivity. And only at graphene content of 5 wt. % conducting cluster starts forming. Quantitative microanalysis of carbon and glass elements is conducted; microstructure and electrophysical properties of these films are investigated. Increased content of carbon in the surface layer of the film is determined and volt-amps diagram linearity, which points to the implementation of Ohm's law, is shown and the reducing of electrical resistivity with the rise of temperature is found. TCR is negative and equals $[(-6,3)-(-8,2)] \cdot 10^{-4}$ K^{-1}. A conclusion is drawn on the possibility of graphene application as a conducting phase in thick-film technology.

BARRIER HIGH-TEMPERATURE NON-METALLIC NANO-FILMS ON METALS FOR PREVENTION OF UNCONTROLLED SPREADING OF METAL SOLDERS

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The possibility was investigated of application of carbon and aluminum-oxide nanofilms coatings on copper, covar, and niobium as barriers limiting the spreading of low-melting soldering materials like tin and lead, as well as mid-melting silver and germanium, and even more refractory copper and nickel. The minimum thicknesses values were determined of carbon and aluminum-oxide films able to completely limit the spreading of the solders mentioned above over the surfaces of metals coated with the non-metallic nanocoatings under investigation.

The dependence was established of wetting threshold of barrier carbon and oxide-aluminum films deposited onto copper by low-melting metals like tin and lead from their thickness upon heating of films in the temperature range $250 \div 600$ °C.

Changes were studied in the structure of carbon and aluminum-oxide barrier films of various thickness on copper, as well as of aluminum-oxide films on the covar and niobium upon annealing .

them within the temperature range $950 \div 1460$ °C.

The suitability was determined of carbon films on copper, as well as for aluminum-oxide films on the covar and niobium, to serve as a barrier for the prevention of spreading of molten germanium, silver, and Psr-72 solder.

The unsuitability was found of alumina films on the covar to serve as a barrier to prevent the spreading of molten copper, as well as of alumina films on niobium – to prevent the spreading of molten nickel.

On the basis of results of the studies carried out, carbon and alumina films $50 - 100$ nm thick were recommended for practical application in precision copper brazing using tin, silver and copper-silver solders; as well as aluminum-oxide films of the same thickness on the covar – for brazing by silver and copper-silver solders, and aluminum-oxide film up to 200 nm thick on niobium – for brazing by silver, copper-silver and copper solders

KINETICS OF HEAT FLOWS TO ELECTRODES during ELECTROSPARK DEPOSITION OF COATINGS

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Calculation of heat flows was carried out on the basis of the thermal equation solution, which enabled to establish the correlation between the electrode temperature and the power of heat flow [Ref.]. The measurements of the electrodes temperature were performed by tracing the signal from thermocouples at different parameters of the electrospark deposition process.

The figure below shows the intensity of heat flows to anode (Q_a) and cathode (Q_k) depending on spraying duration at different pulse off-duty ratio: 16.8 (1); 17.0 (2); 16.2 (3); 17.4 (4).
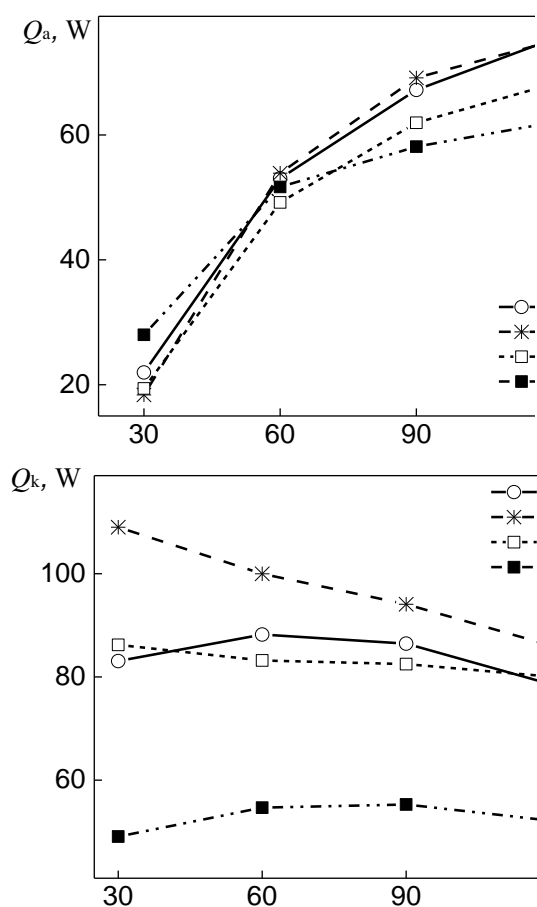
of interelectrode gap. This is consistent with the hypothesis of positive ions layer near the cathode surface, which take part in the occurrence of cathode jets.

The time dependence of heat flows to the electrode and the substrate substantially differs. This is explained by the fact that the intensity of active zone heating is determined by two main processes: ohmic heating and cathode jets action. The contribution of each process to the cathode and anode heating is different and varies depending on the parameters of the deposition process.

There is detected at least two modes of electrospark deposition, which definitely differ in intensity of heat flows to the anode and cathode. The obtained electrospark coatings have properties and character of formation that corresponds to a specific mode.

It is established that the thermal kinetics of electrode active zones significantly changes during the process of coatings growing. This indicates that the heat flows intensity to the electrodes depends on the state of electrode`s active surface and the evolution of layer during the deposition process. Variation with electric and geometric parameters of deposition enables to realize discrete heat modes of mass transfer and to control the process of electrospark coating formation.

The concept of gradual adjustment of deposition parameters, based on the layer thickness and the electrodes heat regime, is proposed to provide controlled formation of the electrospark coatings gradient structure.

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It is established that in the process of electrospark hardening the voltage between anode and cathode practically does not depend on the size

INCREASE OF TRIBOTECHNICAL CHARACTERISTICS OF TITANIUM ALLOY VT9 FOR THE NITROGEN ACCOUNT

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The problem of increasing the level and stability of the mechanical properties of structural titanium alloys is currently one of the most pressing problems of aircraft and engine construction. Important is the issue of maintaining high plasticity, toughness and simultaneous increase in strength, wear resistance. All this led to the need to develop technologies for hardening and protecting surfaces of products of various kinds with coatings. The aim of the work was to increase the tribotechnical characteristics of the titanium alloy VT9 due to nitriding.

Nitriding of the titanium alloy VT9 was carried out at a temperature of 950 ° C for 2 hours. In addition, titanium hydride 16 g / m2 saturating surface was introduced into the reaction medium. The titanium hydride decomposes at temperatures above 400 ° C to form atomic hydrogen. As is known, hydrogen activates the process of nitriding of transition metals[1].

When nitriding the titanium alloy VT9 without additional activation of the process by hydrogen, a coating consisting of titanium nitride with a thickness of 2 μm was formed on the surface.

In the case of activation of the nitriding process with hydrogen, a layer of TiN nitride (a = 0.42342 nm) with a thickness of 3.0-3.5 μm, microhardness (15.5-16.0) GPa was formed on the surface of the sample from VT9 alloy. Underneath it is a solid solution of nitrogen in α-titanium (a = 0.29284 nm, c = 0.46978) with a thickness of 30-35 μm.

The study of wear resistance was carried out on a 2070SMT-1.

The material of the counter body is hardened and tempered steel U8A in the form of a disk (R = 25mm, h = 10mm), the surface hardness was 62 HRC. The speed of rotation of the counter body is 2 and 3 m / s, the load is 2 kg. The test time of each sample is 3 minutes. From the data obtained, it follows that after nitriding, an increase in surface wear resistance and a change in the mass of the treated and untreated samples are observed. At a speed of rotation of the counter body - 200 rpm, for the samples nitrided without activation of the saturation process, the tribotechnical characteristics increased by 1.7 times. For nitrated with activation - in 2,4 times. In the case of an increase in the speed of rotation of the counter body to 300 rpm: nitrided without activation - an increase of 7 times; nitrated with activation - 16.8 times. The change in mass is explained by the fact that on the untreated surface the setting processes develop, and on the processed surface, mechanical wear.

The setting processes are characterized not only by an increase in wear resistance, but also by intensive formation of tears and breaks on the contacting surfaces alternating with each other. It is also observed that the titanium alloy adheres to the surface of the counter body, smeared it in the direction of motion, which indicates an intensive development of plastic deformation in the surface layers. Surface deformation, as noted in [2] in this case, contributes to the formation of juvenile friction surfaces, their convergence, the formation of metal bonds and determines the intensity and nature of the friction surface destruction.

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THERMODYNAMICS OF DIFFUSION HEATING OF TITANIUM AND TITANIUM ALLOYS WITH NITROGEN, CARBON AND OXYGEN.

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High strength, low density and good corrosion resistance are the main properties that make titanium and its alloys widely used in the aviation, automotive, chemical and medical industries. At the same time, the use of titanium without special surface treatments is impossible in certain cases. Creation of new complex coatings of the methods of their application is possible subject to the study of chemistry and the thermodynamic conditions of such processes, as well as the analysis of the equilibrium composition of the system involving the main components of the mixture, used to saturate and components of the original alloy, which is processed.

The reactions of the formation of carbides, nitrides and titanium oxides, which proceed with the saturation of titanium and titanium alloys with carbon, nitrogen and oxygen, were calculated.

In conducting calculations of more than 800 chemical reactions, the possibility of presence in the reaction space of chlorides, oxychlorides and other titanium compounds of different valences, carbon, its oxides (CO, CO_2), nitrogen, oxygen, products of their interaction with each other and chlorine ($COCl$, $COCl_2$, NCN , NCO, NO, N_2O, NO_2, NO_3, N_2O_3, N_2O_5, $NOCl$, CO_2Cl), and in reaction products Titanium titanium carbide TiS, titanium nitride TiN, titanium oxides (TiO, TiO_2, Ti_2O_3, Ti_3O_5, Ti_4O_7), carbon oxides. The calculations were carried out using the HSC CHEMISTRY program.

The analysis of the given data shows that when saturation of titanium and titanium alloys with carbon, nitrogen and oxygen, it is possible to form a diffusion layer consisting of carbide, nitride and titanium oxides. Moreover, the highest thermodynamic probability of formation in the diffusion layer of titanium carbide TiC and TiO_2 oxide. The formation of titanium nitride TiN in the introduction of nitrogen is most likely due to the exchange reaction from the TiC carbide.

To analyze the physical and chemical conditions of saturation, a thermodynamic approach based on the determination of the equilibrium composition of a closed system was used. We can assume that the results of calculations model the composition of the reaction medium for a certain content of the corresponding reagents. The calculations were carried out using a standard program with a database of thermodynamic data that allows searching for the equilibrium composition of a closed system with a maximum entropy.

The equilibrium compositions of the reaction medium were studied at different ratios of the initial components (Ti-Cl-C, Ti-Cl-C-N, Ti-Cl-C-O-N, Ti-Cl-C-ON, Ti-Cl-C -ON) The influence of hydrogen on the thermodynamic probability of the chemical reactions occurring and the composition of the gas and condensed phases in the reaction medium is also considered.

The analysis of the data obtained on the chemistry and thermodynamics of the processes proceeding and the determination of the equilibrium composition of the reaction enviroment in a wide temperature range allows us to reasonably approach the development of a new method and the establishment of a rational flow of the starting reagents at the complex saturation of titanium and titanium alloys with carbon, nitrogen and oxygen. Calculations have shown that in the presence of hydrogen, the reaction of formation of nitride and titanium carbide is more likely than similar reactions without its participation.

Experimentally confirmed the possibility of applying to the surface of titanium and titanium alloys of complex coatings involving carbon, nitrogen and oxygen. Depending on the composition of the initial components used to create the reaction enviroment, titanium nitride, Titanium nitride, Titanium titanium carbide, tungsten carbide and titanium nitride - TiC and TiN, titanium and Titanium oxide titanium nitride - TiS form, are formed on the surface of titanium and titanium alloys, Ti02, TiO. Under the coating is the zone of solid solution of saturation elements (N, C, O) in titanium, the thickness of which depends on the temperature and the saturation time.

Materials in the $Ln^I_2O_3$–$Ln^{II}_2O_3$–$Ln^{III}_2O_3$ systems , where Ln^I, Ln^{II}, Ln^{III} – lanthanides, for thermal barrier coatings

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Thermal barrier coatings (TBC) are widely used in modern gas turbine engines to reduce temperature of metal surfaces in turbine sections and combustion chambers in order to increase their lifetime and prevent degradation of the main material. Requirements for materials of the upper ceramic coating of TBC are as follows: low thermal conductivity < 2 W/(m·K); high coefficient of thermal expansion; phase stability between room and operating temperatures; sintering stability at high temperatures; low Young module; erosion resistance. In the upper coating layer up to 1200 °C, ZrO_2 stabilized with Y_2O_3 (YSZ) is used as a metastable t' modification. To date, material meeting all of the above-mentioned criteria at a service temperature of more than 1200 °C was not found. In developing new materials for the upper ceramic layer of TBC, there are two main approaches. One focuses on a solid solution of ZrO_2–Y_2O_3–lanthanide oxides. The other one relates to zirconates of REE with a pyrochlore-type structure that are characterized by phase stability up to melting temperatures.

The special role of lanthanides oxides is in the stabilization of zirconium dioxide. The ZrO_2 transformation reinforcement mechanism was established with the help of the construction of the phase diagram of the ZrO_2-Y_2O_3 system [1]. The further construction of the phase diagrams of the systems involving of other lanthanides oxides allowed establishing the concentration dependences of the areas of monoclinic (M), tetragonal (T) and cubic fluorite-like (F) structures of zirconium dioxide [2].

Simultaneous doping of zirconia with several stabilizers Ln_2O_3 (Ln=lanthanides) put on the agenda the question of the effect of the number and percentage of these stabilizers on the width of phase fields M-, T- and F-phases in the binary systems ZrO_2-Ln_2O_3. These data are important for creation of modern structural and functional materials, in particular for obtaining targets when thermal barrier coatings deposition in advanced gas turbine engines.

Interaction in binary and more component systems involving lanthanide oxides and the construction of phase diagrams of such systems will answer the question of new phase's formation based on ternary compounds, their interaction with other phases of the system, and the width of phase fields with different structure of lanthanide oxides.

In this work, the interaction prediction in the ZrO_2-Ln_2O_3 systems (Ln=lanthanides) and $Ln^I_2O_3$–$Ln^{II}_2O_3$–$Ln^{III}_2O_3$ was made and the experimental data that confirm the prediction were obtained.

The samples were synthesized from ZrO_2 and Ln_2O_3 powders of "Ч" grade by mechanical mixing method in ethanol media. The composition of the samples varied in a wide range. After evaporation of the alcohol, the mixtures were fired in air at 800 °C for one hour to remove liquids residues and organic matters, as well as preliminary reaction of the components. The mixtures were then grounded in an agate mortar and pressed uniaxially into pellets of 5 x 5 mm in size, which were annealed in air at 1400 °C for 12 hours.

After cooling, the samples were analyzed by X-ray diffraction (XRD) (DRON-3M, CuKα-radiation, Ni-filter). The samples were repeatedly grounded in an agate mortar, pressed into pellets, annealed under the same conditions and subjected to XRD. The uniformity of diffractograms indicated an equilibrium at 1400 ° C.

The data on interaction in ZrO_2–Ln_2O_3 and $Ln^I_2O_3$–$Ln^{II}_2O_3$–$Ln^{III}_2O_3$ systems, where Ln=lanthanides, are presented in the work.

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СТРУКТУРА И СВОЙСТВА ГАЗОТЕРМИЧЕСКИХ ПОКРЫТИЙ НА ОСНОВЕ ИНТЕРМЕТАЛЛИДОВ СИСТЕМЫ Fe-Al

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Интерметаллиды железа Fe_3Al и $FeAl$, которые обладают высокой жаростойкостью при 600-1000°C, сопротивлением коррозии в агрессивных серосодержащих средах и изнашиванию, представляют собой перспективный материал для разработки новых защитных покрытий. Однако недостатком интерметаллидов железа являются их низкие пластичность и сопротивление удару при комнатной температуре, недостаточное сопротивление ползучести в области умеренных температур.

На основании материаловедческого анализа диаграмм фазового равновесия многокомпонентных систем с участием Fe и Al были выбраны легирующие элементы (а именно Ti, Mg, Cr, Zr и La) и разработаны составы покрытий с повышенными по сравнению с интерметаллидами системы Fe-Al механическими и физико-химическими свойствами.

Порошки для нанесения газотермических покрытий получали методом механохимического синтеза (МХС), а для получения покрытий методом электродуговой металлизации изготавливали порошковые проволоки.

Для изучения условий формирования покрытий из легированных порошков при плазменном напылении (ПМ) была использована компьютерная модель CASPSP, а изучение физико-химических процессов, которые при этом происходят, проводили путем анализа поведения частиц материала на последовательных стадиях процесса ГТН: при прохождении в объеме газовой струи (путем сбора частиц в водяную ванну), при деформации в момент удара об основу (сплет-тест), при формировании слоя покрытия.

Анализ физико-химических и теплофизических процессов в условиях детонационного напыления (ДН) был проведен с привлечением метода математического планирования эксперимента и регрессионного анализа результатов эксперимента.

Одним из способов улучшения механических характеристик Fe-Al интерметаллидов является перевод этих материалов в наноструктурное состояние.

В связи с этим было проведено исследование формирования газотермических покрытий с предварительным переводом порошка в наноструктурное (8,8 нм) и аморфное состояние на этапе механо-химического синтеза.

Полученные разными методами Fe-Al покрытия были исследованы с определением их износостойкости (абразивной, газоабразивной), жаростойкости, коррозионной стойкости. Механические характеристики покрытий были определены методом микроиндентирования.

По комплексу характеристик разработанных интерметаллидных FeAl-покрытий, обладающих высокой жаростойкостью при 700°C, коррозионной стойкостью в средах 3% NaCl, $0{,}5M H_2SO_4$, сопротивлением газоабразивному изнашиванию при 550°C, они могут быть рекомендованы для практического применения для защиты от окисления, коррозии и газоабразивного изнашивания узлов котлов ТЭЦ и мусоросжигающих заводов. Они являются прспективными для участия в решении проблем теплоэнергетики в части повышения температуры перегретого пара (до 600-650°C), что позволит повысить КПД паровых турбин, и переходу на пониженный коэффициент излишка воздуха на процесс горения, что позволит решить экологическую проблему снижения выброса NO_x в атмосферу и вместе с тем уменьшить развитие низкотемпературной коррозии в теплоагрегатах.

STRUCTURE AND PHASE COMPOSITION OF MICROPLASM COATING FROM $Ti_{60}Cr_{30}Al_3Si_2(SiO_2)_5$ ALLOY

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Quasicrystals and their approximants are promising materials for use as coatings, becouse they have high hardness and low friction coefficients. The authors [1] by the methods of gas-thermal spraying of the three-component $Ti_{60}Cr_32Si_8$ alloy in air with the presence of oxygen and plasma spraying in air and in vacuum, tried to obtain a coating with a quasicrystalline icosahedral structure. All obtained coatings contained a doped solid solution based on β-Ti and the Lavase $TiCr_2$ phase, and when gas-thermal and plasma spraying in the air, a large number of oxide phases were observed.

The aim of this work is study the structure and phase composition of coatings $Ti_{60}Cr_{30}Al_3Si_2(SiO_2)_5$ obtained by microplasma sputtering.

The $Ti_{60}Cr_{30}Al_3Si_2(SiO_2)_5$ alloy was melted from high purity elements in an arc furnace MIFI-9-3 in an atmosphere of high purity argon. High-purity fused silica SiO_2 was used for high-quality oxygen input during the melting of alloy.

The coating was applied to a steel substrate using a microplasma spray method in an atmosphere of air. The phase composition of the initial state and the resulting coatings were investigated by X-ray analysis (DRON-UM1) in monochromatic Cu-radiation. As a monochromator, a single crystal of graphite was installed, mounted on a diffracted beam. Data processing was performed using the PowderCell 2.4 program.

In initial state $Ti_{60}Cr_{30}Al_3Si_2(SiO_2)_5$ alloy has two phase and contains an 1/1α(TiCrSi) (78% mass) approximant of the quasicrystalline phase and $TiCr_2$ (Fig. 1,a). In the resulting plasma coating, up to 30% mass Approximant 1/1α(TiCrSi) is fixed, and the main phase is titanium mononitride TiN (52% mass).

Since this coating is thin, on the diffractogram the reflexes from the substrate with the fcc structure of the stainless steel (Fig. 1, b) are fixed. The presence of TiN in the coating is promising since it is known that the materials on its basis are characterized by high wear resistance

indexes, which is why they are widely used to reduce the coefficient of friction.
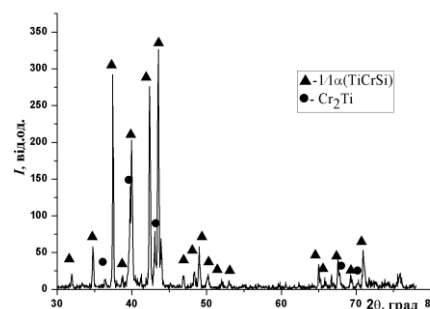
a
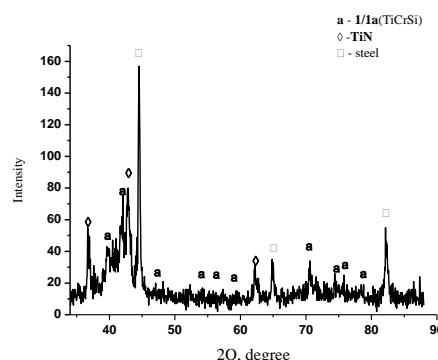
b

In order to determination of the mechanical properties of the coating the method of automatic indentation was used   It is determined that the hardness of the coating is 5.5 GPa, and the elastic modulus is -165 GPa.

The results demonstrated the fundamental possibility of using an $Ti_{60}Cr_{30}Al_3Si_2(SiO_2)_5$ alloy containing a quasicrystalline phase approximant as a coating material for used at high temperatures and loads, becouse it has a stable phase composition and high mechanical properties.

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ФИЗИКО-МЕХАНИЧЕСКИЕ СВОЙСТВА МНОГОСЛОЙНЫХ ZrN/CrN ПОКРЫТИЙ В ЗАВИСИМОСТИ ОТ ТЕХНОЛОГИЧЕСКИХ ПАРАМЕТРОВ ПРОЦЕССА ИХ ФОРМИРОВАНИЯ

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Промышленное внедрение тонких покрытий на основе ZrN, используемых в машиностроении, ремонтной и инструментальной промышлености для упрочнения режущего инструмента и пар трения ограничиваетсяудовлетворительным сочетанием их трибологических (износостойких и антифрикционных) и физико-механических свойств[1]. Решение возможностей и областей применения пленок на основе ZrNвозможно за счет осаждений многослойных структур с использованием CrNв качестве второго чередующегося слоя [2].Геометрия многослойной структуры, состоящей из чередующихся слоев, позволяет получать дополнительный эффект,который возникает в результате произведения свойств отдельных слоев, составляющих структуру. Цель работы – установления зависимости технологических условий формирования многослойных ZrN/CrNпокрытий методом вакуумно-дугового осаждения и их механических свойств.

Многослойные ZrN/CrNпленки на поверхность тестовых образцов из стали12Х18Н10Т ($20\times20\times2$ mm^3) осаждали методом вакуумно-дугового испарения двух однокомпонентных катодовиз циркония и хрома в активном газе азота (99,95 %)при различном сочетании технологических параметров: ток дуги (I_d)составлял 100 А, давление азота (P_N) варьировалось в диапазонеот 0,029 до 0,43Па, расстояние от испарителя до подложки – 250 мм, температура подложки (T_S)– 250 ℃, постоянный отрицательный потенциал ($-U_S$) был в интервале –70 и –150 В.

Морфологические особенности поверхности и сечения пленок изучали на сканирующем электронном микроскопе FEI Quanta 400. Фазовый состав определялся по дифрактограммам, полученным в Cu-Kα-излучении с участков пленок с использованием рентгеновского дифрактометраPanalyticalX'PertD.Микротвердость композиций определяли на микротвердометреStruers Duramin-5 с нагрузкой в 25 кгс.

Полученные многослойные покрытия имеют крупноячеистую поверхностную структуру. Наблюдается значительное количество микрокапельной фракции, средний размер микрокапель составляет 6 мкм.На РЭМ-снимках боковых сечений просматривается однородность чередующихся слоевZrN (светлые) и CrN (темные).Хорошо видно, что сначала слои повторяют рельеф подложки, но по мере роста пленкислои выравниваются. Известно, что большую роль в механических свойствах покрытий играет граничная структура между подложкой и покрытием. В исследованных образцах хорошую адгезию покрытия и подложки обеспечивает переходной слой шириной 0,3–0,45мкм.Анализ рентгенодифракционных спектров многослойных покрытий показывает наличие двух фаз ZrN и CrN, соответствующих формируемым слоям. Преобладающим типом текстуры является [200]ZrN для всех образцов.

Установлено, что отрицательный потенциал смещения и рабочее давление комплексно влияют на механические свойства покрытий. При P_N= 0,43 Па формируется пленка с максимальным значением микротвердости4685HV0,025.При малых P_N= 0,029 Па и росте $-U_S$до –150 Взначение микротвердостиуменьшается до 2795HV0,025.

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DIFFUSION HEAT-RESISTANT COATINGS FOR STEELS 08Ch17T AND ST. 45

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The most promising diffusion methods for obtaining heat-resistant coatings on steels include the processes of aluminizing and chromoalitizing [1]. In addition to heat resistance, the diffusion saturation of the surface of metals and alloys with aluminum and simultaneous or sequential saturation with aluminum and chromium leads to an increase in corrosion and erosion resistance. Among the numerous methods of aluminizing and chromoalitizing, the most widely used method is saturation in powder mixtures.

In the present work, we have studied the processes of aluminizing and chromoalitizing steel 08Ch17T (used for external secondary radiators for recuperators) and steel St. 45 (to clarify the possible replacement of alloy steel on carbon).

The processes of aluminizing and chromoalitizing were carried out in special containers with a fusible gate at a temperature of 900-950 ° C for 2-5 hours. The main components of the powder mixtures were:

a) powder of aluminum powder (aluminum source for aluminizing), a mixture of chromium and aluminum powders (with chromoalination);

b) powder of AlF_3 aluminum fluoride (process activator);

c) alumina powder (an inert additive that prevents sintering of aluminum powder particles and a mixture of aluminum and chromium);

d) titanium hydride powder (to remove residual oxygen from the powder mixture).

As a result of the examination of the samples after testing at 1000 ° C using X-ray phase analysis and X-ray spectral microanalysis, it was established that during the oxidation process, a thin layer of Al_2O_3 forms on the surface of the samples, under which is the FeAl intermetallide (in the case of aluminizing) or FeAl doped with chromium (in the case of chromoalitizing), gradually transforming into solid solutions. At the same time the area of solid solutions increases in comparison with initial those. Thus, the aluminum content decreases as a result of the formation of the oxide film and resorption in the substrate.

The conducted researches made it possible to establish the regularity of the oxidation process at temperatures up to 1000 ° C, and by constructing parametric heat resistance diagrams [2] to evaluate the durability of protective parts for any temperatures up to 1000° C.

The highest heat resistance in the range of 800-1000 ° C has chromium-plated coatings, which increase the resistance of 08Ch17T steel more than 25 times at 1000 ° C. The question of replacing 08Ch17T steel with aluminized carbon steel 45 will be resolved after testing the coatings on the secondary radiators of recuperators at the Fire Station of the Institute of Gas of NASU in 2018.

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ТЕРМОСТАБІЛІЗАЦІЯ НАПРУЖЕНИХ ПЛІВОК Si-C-N

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При плазмохімічному осадженні плівкового Si-C-N із гексаметилдісилазану збільшення напруги зміщення сприяє їх твердості [1]. Одним із факторів збільшення твердості є напруженість плівок спричинена підвищенням швидкості нанесення матеріалу, несумісністю матеріалів плівки і підкладки та наклепом зарядженими частинками в зростаючому полі зміщення. Напруженість робить плівку температурно нестабільною. Метою роботи було оцінити величину напруженості через зміну твердості плівки після помірного відпалу у вакуумі. Плівки отримано за режимами роботи [1] на кремнієвих підкладках КДБ–7,5 осадженням при різних напругах зміщення на підкладці (U_d): -5, -100, -150 та -250 В. Осаджені плівки відпалювали у вакуумі при температурі 600°C упродовж 120 хв. Дослідження велись за методиками XRD, FTIR та тестуванням твердості по Кнупу.

Після відпалу структура плівок залишається рентгеноаморфною. Твердість плівок, осаджених при $U_d = - 250$ В після відпалу помітно зменшується, тоді як твердість плівок отриманих при $U_d = -5$, -100 і -150 В суттєво не змінюється (Рис. 1).
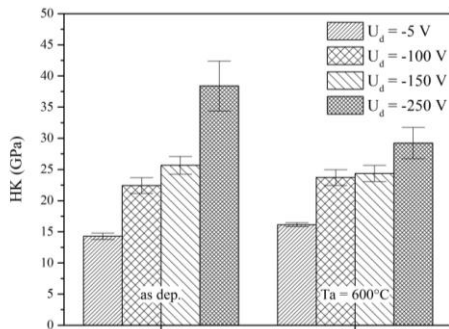
Рис. 1. Твердість за Кнупом плівок Si-C-N осаджених при різному зміщенні на підкладці та відпалених при 600°C

Із FTIR спектрів (Рис.2) плівок осаджених при U_d=-250 В помітно зменшення інтенсивності поглинання у високочастотному крилі широкої смуги пропускання (~1251cm^{-1}) відпалених зразків в порівнянні з не відпаленими. В цій області знаходяться C-N і Si-CH$_3$ зв'язки [2].
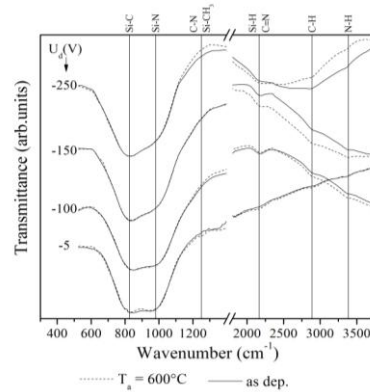
Рис. 2. FTIR спектри осаджених при різному зміщенні і відпалених Si-C-N плівок

Вони властиві для sp^3 гібридизації і сприяють створеню великих внутрішніх напружень в плівках [3]. Руйнування цих зв'язків і їх перерозподіл може спричиняти формування нанорозмірних порожнин [4], що очевидно також зменшує твердість плівок. Враховуючи те, що Si-H є слабшими зв'язками в порівнянні з C≡N [5,6], поглинання при 2180 см$^{-1}$ є суперпозицією двох типів зв'язків де переважає C≡N компонент. Таким чином, сильно зв'язані атоми азоту і вуглецю, пом'якшують аморфну матрицю, зменшують внутрішні напруження в об'ємі плівок, що збільшує їх термічну стабільність [7].

Отже, осаджені при $U_d = -250$ В плівки Si-C-N помітно напружені, що додає до їх твердості. Відпал при 600°C знімає напруженість, а заодно зменшує та стабілізує твердість. Це можна використати для осадження та відпалу плівок в одному технологічному циклі. Можливо, при осаджені плівок при температурі вище 500^{0}C не буде потреби в додатковому відпалі для зняття напруженості плівок Si-C-N, але це потрібно дослідити.

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TOPICS 4 (D)

Nanostructure refractory compounds

ELECTRIC, THERMOELECTRIC AND MAGNETIC PROPERTIES OF FERROMAGNETIC NANOCOMPOSITES FORMED BY MATRIXES Al$_2$O$_3$ AND SiO$_2$ WITH DISTRIBUTED IN THEM Co NANOPARTICLES

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Ferromagnetic nanocomposites (FMNC) represent magnetic nanoparticles distributed in a dielectric matrix. The scientific and technical significance of such materials is due to the fact that by the technological control of the size, concentration and shape of the ferromagnetic single-domain nanoparticles it is possible to give FMNC necessary properties.

FMNC with ferromagnetic Co nanoparticles in dielectric matrixes Al$_2$O$_3$ and SiO$_2$ were grown by the method of two-crucible electron beam evaporation in the form of thin layers with thickness $(0{,}8 \div 3)$ μm on polycor substrates.

Electrical, magnetic and thermoelectric properties have been studied in the temperature range $5 \div 290$ K and in magnetic fields up to 5 kOe.

For both dielectric matrixes transmission and scanning electron microscopy were carried out which showed that in the case of FMNC Co/Al$_2$O$_3$ nanoparticles (NP's) with sizes of 10-20 nm and in FMNC Co/SiO$_2$ - 7-13 nm are observed. With increasing of the Co concentration dimensions of NP's increase.

The temperature dependences of the FMNC resistivity with different matrixes were measured. In the Mott coordinates $\ln(\rho/\rho_{77}) \propto (1/T)^{1/4}$ in the temperature range 95-290 K this dependence is linear and is explained by the hopping mechanism of electrons transport with variable jumps length over localized states.

We observed for the first time the giant positive thermoelectric power in a magnetic field for the FMNC Co/Al$_2$O$_3$. A mechanism is proposed for the appearance of a spin-dependent giant positive thermoelectric power in a magnetic field under conditions of a hopping type of electron conductivity over nonmagnetic localization centers, based on the effect of reducing the scattering of electrons by the presence of magnetic centers due to the parallel direction of the magnetic moments of electron spins and magnetic moments of these centers when the magnetic field is switched on [1].

In the case of the SiO$_2$ matrix a negative magnetothermoelectric power is detected as a result of the chemical interaction of Co and SiO$_2$. This creates a mixture of nanoscale ferromagnetic silicides of cobalt and antiferromagnetic CoO, which causes spatial fluctuations of their magnetic moments, leading to an increase electrons scattering.

From the magnetic characteristics of the FMNC with different matrices, the temperature of the transition to the spin glass state is determined. For the SiO$_2$ matrix it is shifted toward higher temperatures (50 K). Unlike Co/Al$_2$O$_3$, the Co/SiO$_2$ composite exhibited significantly less coercive force which is also the result of the influence of the silicide phases of cobalt and antiferromagnetic CoO.

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KINETICS AND THERMODYNAMICS OF WATER VAPOR ADSORPTION ON MOLYBDNUM DISULFIDE MICRON POWDERS

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Now intensive studies are carrying out of new 2D multi-functional nanomaterials design which based on graphene-like dichalcogenides of d-transition metals, in particular, $2H-MoS_2$ nanoparticles ("few-layers") or monolayers. Actual tasks include following: the design of high sensitive gas nanosensors, incl. moisture; control semiconductor properties which are depending on the features of real 2D nanostructures and the state of their surface.

Aim of the studies: kinetic and thermodynamic characteristics of adsorption and desorption processes for water vapor on micron powders and graphene-like nanoparticles of layered $2H-MoS_2$. The present report presents the results for $2H-MoS_2$ micron powders.

It is known that when the adsorption properties of surface-active materials are analyzing, an important task is to elucidate the peculiarities of the interaction of adsorbate with the adsorbent, nature of the interaction forces at the interface which determine the adsorption activity of the adsorbent, and the kinetics of macro- and microprocesses.

The obtained results make it possible to characterize the course of desorption of water molecules from the adsorbent when the relative humidity decreases from 100 to 60% in the reaction system (Fig. 1, curve 1). The sensitivity of the adsorption system is characterized by the rate (w) of the desorption process (Fig. 1, curve 3). The maximum saturation of the water vapor adsorbate at 100% relative humidity, the degree and rate of its entrainment under conditions of humidity change (up to 60%). Kinetic data of adsorption characterizing the degree and rate of saturation of 2H-MoS2 with an increase in humidity from 60 to 100% are presented (Fig. 1, curves 2, 4).

On the potential theory basis it was estimating the binding energy of water molecules with a non-homogeneous porous MoS_2 structure is performed. Dependences of the adsorption forces of the adsorbate-adsorbent, the equilibrium pressure of water vapor over the surface of the adsorbate, associated with the adsorbed volumetric amount of water, are presented. Based on the experimental relationships, the binding energy of the adsorbed water volume was estimated.

On the experimental and calculated data basis water vapor adsorption isotherms have been constructed (V = f (p), 15-50 °C). The values of true adsorption with a high binding energy were determined, estimates of the parameters of capillary condensation of water vapor with different characteristics of adsorbate porosity were identify. The curve of the dependence of adsorption on the water vapor pressure has an S-shape with an inflection point of about 15 mm^3 which corresponds to the true adsorption of $2H-MoS_2$ micron powders on the adsorption active surface ($\approx$ 17% of the total volume).

The obtained results will be used for a comparative analysis of adsorption and desorption processes of water vapor on graphene-like $2H-MoS_2$ nanoparticles at design of gas nanosensors of moisture based on them.
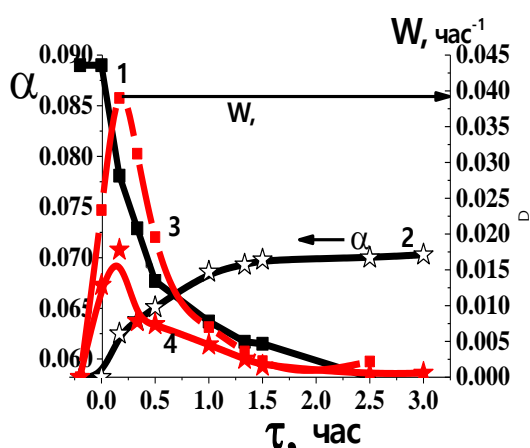
Fig. 1. Kinetic dependences of the reduced mass (α) and water desorption rate (w) for $2H-MoS_2$ micron powders at 15 ° C: 1, 3 - desorption (relative air humidity - 60%); 2, 4 - adsorption and adsorption rates (relative humidity - 100%).

SIMULTANEOUSLY SYNTHESIS OF O-DOPED CARBON NITRIDE AND WATER-SOLUBLE CARBON NITRIDE OXIDE FROM CYANURIC ACID AND UREA MIXTURE

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Graphite-like carbon nitride (and its nanostructured and doped, in particular, by oxygen, derivatives), characterized as a non-toxic and chemically highly resistant material, attract special attention as the promising photocatalyst for green energy. Doping of carbon nitride by oxygen significantly improves its photocatalytic properties (5 times accelerates the photodegradation of methylene blue and 2 times accelerates the evolution of H_2) [1]. The simultaneously synthesis of water-soluble carbon nitride oxide $(g\text{-}C_3N_4)O$ (16% O) and insoluble oxygen-doped carbon nitride $(O\text{-}g\text{-}C_3N_4)$ (7% O) carried out by thermal treatment of cyanuric acid and urea mixture (in 1:1 ratio). Synthesis was realized under ambient pressure without the use of additive carrier gas (N_2 or Ar). The retainable pyrolysis-generated self-supporting atmosphere and the reaction temperature (550°C) are two necessary conditions. Previously, O-doped carbon nitride and nitride oxide were synthesized by us from a single precursor – melamine [2] or urea [3]. In addition, a group of European scientists later synthesized carbon nitride oxide (CNO) from urea under ultra-high pressure conditions (3 GPa) in a diamond anvil [4].

The reduction of the synthesized (from cyanuric acid and urea mixture) samples of carbon nitride oxide (CNO) was carried out on a technique described for the reduction of graphite and graphene oxides by hydroquinone [5]. According to the results of XPS and IR spectrometry (Fig. 1b) the chemical bonds between atoms in a heteroatomic plane of reduced carbon nitride (RCN) correspond to the bonds in a synthesized carbon nitride (SCN). However, according to XRD results (Fig. 1a), RCN, which consists of poorly connected heteroatomic azagraphene layers, has a significantly larger (on 0.09 nm) interplanar distance between the adjacent nitrogen-carbon layers than interplanar distance between the layers of SCN (Fig. 1c).

It was found that the pyrolysis of mixture of different precursors (cyanuric acid and urea) yielded product with smaller crystalline domains but larger surface (and, consequently, with a higher catalytic activity) areas compared to that of melamine or urea.
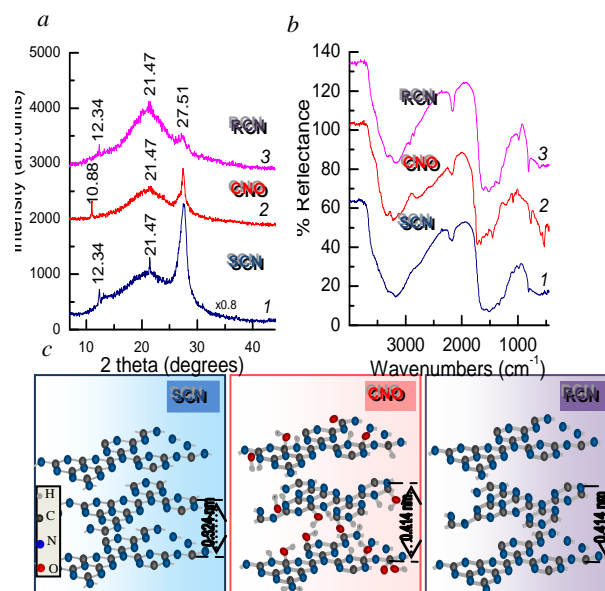
Fig. 1. XRD patterns (*a*) and IR spectra (*b*); schematic atomic model of the layers and interplanar distances between adjacent layers (*c*) of reduced carbon nitride (RCN), oxide carbon nitride (CNO) and synthesized carbon nitride (SCN).

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DAMPING PROPERTIES OF THE DIAMOND NANOCOMPOSIT WITH ADDITIVES OF TUNGSTEN OF VARIOUS GENESIS

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When creating new tool materials, especially at the stage of quality optimization and working out of sintering conditions, an important role is played the quality assessment of the obtained samples. The most promising methods for such assessment are non-destructive testing methods. Among these methods, the most useful information about the quality of sintering can be obtained by measuring the damping characteristics (damping decrement), since they are sensitive to porosity and the presence of defects at the grain boundaries. Especially useful this method can be for composites consisting from nanoparticles, because they have a large area of grain boundaries, the study of which is problematic by optical methods.

The aim of this work is to determine the relationship between the damping characteristics and the physicomechanical properties of composite samples on the basis of diamond nanopowder with addition of tungsten nanopowder from various genesis, sintered at different temperatures.

Methods of research. To prepare the samples, a diamond nanopowder of static synthesis ACM5 0,1/0 was used in the delivery state. Tungsten-containing additives of various genesis were introduced into the powder. Additives I, II, were obtained by an electric spark method from tungsten wire in the distilled water and ethyl alcohol, respectively. In the case I, the particles contain different tungsten oxides, II – particles are pure tungsten core surrounded by tungsten carbides (W_2C and WC). Addition III – tungsten powder (W). The metal from oxide was reduced by annealing the prepared mixtures in a hydrogen medium. In the production of particles by the method of electrospark dispersion they have a spherical shape with a wide distribution in size 0,5-5 microns.

As an estimate of the damping ability of the material, the value of logarithmic decrement δ, which was determined by the resonance method, was used. To implement the method in the V. Bakul Institute for Superhard Materials of the National Academy of Sciences of Ukraine, an automated system was developed on the basis of the measuring stand "Sound-107" [1].

The results of studies damping characteristics of diamond-tungsten carbide nanocomposites with various additives showed that for nanocomposites with the addition of W, W_2C, WC (II), an increase in the sintering temperature led to an increase in the logarithmic decrement δ. For nanocomposites with the addition of tungsten oxides(I) and pure tungsten W (III), an increase in the sintering temperature to 1840 and 1785 °C, respectively resulted in decrease δ, but with a further temperature increase up to 1900 °C, the logarithmic damping decrement increased.

The minimum values of the damping characteristics were observed at the sintering temperature 1750-1850 ° C. The low values of the damping properties in this range of sintering temperatures indicate that the samples obtained have a low porosity and a minimum number of defects, which is very important for cutting materials.

For diamond-tungsten carbide nanocomposites with the addition of W, W_2C, WC, a correlation was established between logarithmic damping rate, crack resistance, and hardness of the samples. Higher values of nanocomposites hardness corresponded to smaller values of the logarithmic damping decrement. An increase in the sintering temperature caused an increase in the fracture toughness and logarithmic damping decrement of nanocomposites with the addition of W, W_2C, WC.

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THE EFFECT OF FEAL POWDER MODIFICATION ON THE PROPERTIES OF D-GUN COATINGS

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Combination of high elevated temperature strength, excellent corrosion resistance in oxidising, sulphidising or carburising environments up to 1000 °C, relatively low density as compared with stainless steels and nickel superalloys as well as low price of raw materials make FeAl intermetallic alloys attractive materials for medium temperature applications. However, poor room temperature ductility, low creep resistance and sensibility to environmental embrittlement restrict their industrial applications as structural parts. Protective coatings of iron aluminides can be much more attractive alternative.

Self-propagating high-temperature synthesis (SHS) is known as a promising technique for processing intermetallic powders at relatively low costs. The powder of the eutectoid FeAl-FeAl2 composition produced by the SHS [1] was shown to be promising for thermal spraying protective coatings [2-3].

This work aimed at investigating the effect of modification of the synthesized powder structure on the properties of D-gun coatings from it.

The powder was manufactured through a mechanically assisted self-propagating high-temperature synthesis route. Nanosized SiO2 particles were used for the powder structure modification. Detonation spraying was performed on a'Perun-S' detonation gun complex developed in EO Paton Electric Welding Institute of the National Academy of Sciences of Ukraine.

Structural investigations have shown that addition of a small amount of SiO2 to the Fe-Al charge mixture does not lead to the essential change in phase composition of the synthesized powder. Meanwhile, noticeable structure refining of the powder was observed. Thus, thickness of lamellar B2-phase crystals in the as-modified powder was about 200-300 nm as compared to 0.5-1.5 μm in the unmodified one.

Scanning electron microscopy (SEM) with high resolution energy dispersive X-ray analysis (EDX) have shown that silicon formed as a result of aluminothermic reduction of SiO2 with aluminum during the synthesis process is preferentially located in the B2-phase and not practically detected in FeAl2.

D-gun coatings from the modified powder demonstrate good erosion resistance at room and elevated temperatures. Oxide dominated erosion seems to take place in the coatings at 550 °C.

Oxidation kinetics of D-gun coatings from the modified powder at 950 °C in air obeys the parabolic law with the calculated weight gain constant of 1.094 10-7 мг2/(sm4·s). It is essentially less than that of the unmodified powder and is supposed to be connected with promoting α-Al2O3 formation during oxidation and lowering the Fe2O3 content in the oxide scale.

The proposed approach can be considered as an effective route to improve properties of FeAl-based thermal spray coatings. Small additions of silicon seem to be promising for oxidation resistant FeAl coatings and can be of interest to increase the coating's working temperatures.

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SYNTHESIS OF SILICON NITRIDE CUBIC MODIFICATION BY HIGH-TEMPERATURE SHOCK COMPRESSION METHOD

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The experimental results of the synthesis of high-pressure phase of cubic modification - γ of Si_3N_4 by high-temperature shock compression are presented. This γ-Si_3N_4 phase was obtained for the first time at high pressures of static compression [1]. Later, the synthesis of γ-Si_3N_4 was successfully carried out under shock compression conditions of silicon nitride in flat ampoules, using copper as an additive for quenching of the high-pressure phase [2].

In the work presented, shock compression of Si_3N_4 powders was carried out in cylindrical ampoules, while KCl salt was used as the additive. The two schemes for shock waves generation were used: (i) a shock wave was created in ampoule with powder by the impact of a cylindrical flyer; (ii) a high pressure was generated in an ampoule with a central rod by detonation in the explosive layer adjacent to the ampoule wall. Two types of explosives were used for experiments: in case (i) the ammonite type, while in case (ii) it was TG.

Two types of Si_3N_4 powders were used for the samples preparation: type 1 contained β-Si_3N_4 without α-modification impurity (mean particle size was $<L> \approx 10$ μm), and type 2, consisted of a mixture of 90% of $\alpha-$ and 10% of β–phases ($<L> \approx 1$ μm).

The mixtures containing Si_3N_4 starting powders and 80-90% (mass) of KCl were prepared for shock compression. The mixtures had a density of 1.1; 1.35 and 1.6 g/cm^3.

The content of polymorphous modifications of Si_3N_4 in the initial samples and in the products of their shock compression was determined by X-ray phase analysis.

To calculate the pressure and temperature during shock compression of Si_3N_4 + KCl mixtures with different densities shock compression adiabats using the literature data were constructed.

The following regularities in the formation of γ-Si_3N_4 have been established.

1. Maximal degree of the phase transformation (up to 38 of mass %) was obtained for the mixture with a density of 1.35 g/cm^3 and 90% of the additive content for the scheme (i).

2. Maximum yield (up to 83 of mass %) was obtained for the mixture with a density of 1.1 g/cm^3 and the additive content of 85% in the case of the scheme (ii).

3. According to the transmission electron microscopy data, the grain size of γ-Si_3N_4 was 10-100 nm.

4. Calculations of shock compression parameters for different ampoules and different loading schemes showed that in the case (i) of the compression scheme, maximal degree of transition was obtained at 17 GPa pressure and 2900 K temperature, while for the scheme (ii) these parameters were 25 GPa and 3400 K, respectively.

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SOL-GEL SYNTHESIS OF SILICON DIOXIDE DOPED WITH COBALT AND NICKEL

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The purpose of the study is the justification of the method for control of the processes of the structrure formation of silicon dioxide doped with cobalt and nickel atoms during processing its hydrogels by organic solvents at the maturation stage. Hydrogels were prepared by the sol-gel method in an aqueous medium under basic (NH_4OH) catalysis.

In the *first* stage, the polycondensation reaction of ethylsilicates with cobalt and nickel chlorides leads to the formation of polymer structures (metal-silica) built from Si-O-M-O (M – metal) groups. They also contain the corresponding organic fragments formed in the condensation reaction with the siloxane and ethoxy groups of the matrix. This is confirmed by the shift of the absorption band v_{as} (Si-O) in the IR spectra of the synthesized products compared with the corresponding absorption band of silica xerogels v_{as} (Si-O) 1093 cm^{-1} and by thermogravimetric analysis data. Differences in the displacement of the absorption band v_{as} (Si-O) 1093 cm^{-1} are associated with the different thermodynamic stability of the products formed and with different degrees of inclusion of cobalt and nickel atoms into the main siloxane skeleton.

In the *second* stage, when the hydrogels are treated with organic solvents, the processes of formation of polymer inclusion structures based on the host-guest principle are continued: molecules of a more volatile substance, the organic solvent (guest), are built into the gel structure of the metal-silica (host), which leads to the formation of clathrates. If these clathrates have a crystalline structure in which both compounds retain their chemical identity and are linked only by the van der Waals forces, chemical interactions between the components continue for a long time in the gel systems, which determine further structural changes in the system during heat treatment. Thus, in the IR spectra of silica xerogels doped with cobalt atoms and dried at 120 °C, the displacement of the characteristic absorption band v_{as} (Si-O) 1093 cm^{-1} clearly depends on the nature of the organic solvent treated with the hydrogels at the maturation stage.

The nature of the organic solvents used to treat the silica hydrogels doped with nickel atoms and the heat treatment temperature also affect the nature of the final products. This is typical for polisilicanikel which hydrogels were treated with methyl ethyl ketone and dimethylformamide.

The effect of organic solvent on the nature of the structures formed in the second stage of synthesis is also associated with the overall high sensitivity of the metal-silica structures to external factors within the temperature range of their formation (both in the liquid phase and in the wet hydrogel stage containing a significant amount of water and ethanol). Reactivity, donor-acceptor properties, molecular volume, dielectric permeability, ability to by sorbed by gel, steric factors, etc. are also important.

Ethyl silicate gels are spatial clusters and have a three-dimensional structure consisting of fragments of oligomeric type. Gels derived from aqueous solutions contain hydroxyl groups on the surface, and water and hydrocarbon residues, in the form of inclusions, are inside the silica core. Apparently, the organic solvent is actively sorbed by the hydrogel within the clathrates, and, when the temperature is raised, it is removed together with water and residual organic fragments. All these transformations, depending on the nature of the organic solvent, contribute to the different degrees of activation of the final structure.

SINGLELAYERAND MULTILAYER VACUUM-ARC NANOSTRUCTURAL COATINGS BASED ON CHROMIUM NITRIDE

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At present, more attention is paid to the relationship between deposition conditions and the structure of the coating, since coatings are one of the most effective tools for giving the necessary functional properties of the surface (surface engineering).The use of a high-performance vacuum arc method makes it possible to obtain coating materials that can work under conditions of high temperatures and pressures under the action of aggressive media and intense wear.Among the most promising materials that provide good wear resistance and corrosion resistance of blade tools operating at high cutting speeds, chromium nitride is used. Coatings CrN exhibits high temperature stability and have a lower coefficient of friction than TiN, which is currently the most widely used in industry.

The coatings were deposited in a modernized "Bulat-6" vacuum unit, which is additionally equipped with a high-voltage pulse generator. The phase composition, structure and substructural characteristics were studied by X-ray diffractometry (DRON-4). The study of the functional characteristics of the coatings obtained was carried out on the study of hardness and tribological characteristics.

It has been found that in Cr-based condensates that have a relatively low heat of nitride formation, with a pressure increase from $2 \cdot 10^{-5}$Torr to $4.8 \cdot 10^{-3}$Torr, the phase composition changes in the following sequence $Cr \rightarrow \beta\text{-}Cr_2N \rightarrow CrN$. The supply of a high voltage voltage in a pulse form makes it possible to form a preferential orientation of the crystallites with the texture axis [110]. The structure obtained by the pulsed influence makes it possible to increase the hardness of the coating to 32 GPa and reduce the coefficient of friction to 0.32 in the system of diamond coatings made of chromium nitride.

Transition to a multilayer coating structure can not only take advantage of CrN component, but also to achieve higher properties. A comparative study CrN_x/MoN_x systems and CrN_x/TiN_x with different periods of mismatch crystal lattices of the phases in the mating layers in this paper.

It is determined that a two-phase structure of CrN and $\gamma\text{-}Mo_2N$ phases of the structural type of NaCl is formed in the multiperiod coatings of the CrN_x/MoN_x system with a nanometer thickness of the layers. Because of the small difference in periods (less than 0.5%) at $\Lambda<20$ nm, the layers form a coherent interlayer interface (with conformity lattice periods) to minimize interfacial energy. The use of a small negative bias potential $U_b = -20$ V prevents a significant mixing at the interlayer boundaries even at the smallest $\Lambda = 10$ nm. The nitride layers formed under vacuum-arc deposition are under the action of compressive stresses.

It has been established that epitaxial growth is not detected in the CrN_x/TiN_xsystem due to the relatively large discrepancy of the periods (more than 2.5%) in the formation of the same structural components in the layers (CrN and TiN phases of the structural type NaCl) (due to the large deformation factor) the smallest $\Lambda = 10$ nm. The action of the deformation factor on the interphase boundary (which prevents the penetration of defects and the formation of nanocracks) makes it possible to achieve a superhard state.

The hardness of CrN_x/MoN_x multiperiod coatings (up to 40 GPa) is lower than CrN_x/TiN_x (up to 50 GPa). This is due to the higher hardness of the TiN component compared to MoN.

PECULIARITIES OF STRUCTURE FORMING IN THE VACUUM-ARC NANO-PERIOD NITRIDE COATINGS BASED ON ZrN

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The deposition of vacuum-arc coatings occurs under the action of the radiation factor due to the bombardment of the material surface by charged accelerated particles. Vacuum arc methods are characterized by a high degree of ionization and therefore most particles in the source field are accelerated. This determines the relatively high average energy of the deposited particles and their high mobility and the ability to form defects.

Zr-N with a large negative heat of formation -366.6 kJ/mol was chosen as the base system in the work. The great interest that manifests itself to this system is based on its unique combination of high mechanical characteristics with resistance to oxidation and radiation resistance. CrN and MoN with different heat of formation (CrN-118 kJ/mol and MoN-34 kJ/mol) were used as the second layer in multiperiod coatings.

The coatings were obtained by the vacuum arc method on the upgraded "Bulat-6" installation. The pressure of the working (nitrogen) atmosphere during precipitation was $P_N = 4 * 10^{-3}$Torr, the deposition rate was about 2 nm / s. The deposition was carried out from two sources to the surface of samples with dimensions of 20x20x2 mm from austenitic steel 12Cr18Ni10Ti (analog of stainless steel SS 321).

One source was Zr, and the other was Cr or Ti or Mo (depending on the type of multilayer coating). The cathode materials used are: chromium, titanium, molybdenum and zirconium, obtained by electron-beam melting (ELF); Active gas - nitrogen (99.95%). The thickness of the layers in the coating (h) was determined by the holding time at the source and on the average for the layer was 7, 10, 20, 40, 75, and 150 nm, which corresponded to a bilayer period with an average thickness of about 14, 20, 40, 80, 150, and 300 nm. During the deposition process, a constant negative displacement potential (U_b).

The phase composition, structure, and substructural properties were determined by X-ray diffractometry (DRON-4) using Cu-K$_\alpha$ radiation.

To understand the spatial distribution of radiation-stimulated changes in the boundary (interlayer) regions during the deposition of high-energy particles, computer simulation was used in the work. For this purpose, a program based on the approximate method of double collisions, TRIM, was used in the work.

The formation of phases with a cubic fcc crystal lattice (ZrN and γ-Mo$_2$N) in the layers of the multiperiod composition ZrN/MoN and the phases of CrN and ZrN in the layers of the multiperiod composition CrN/ZrN with a period Λ more than 20 nm was revealed.

At Λ = 20 nm (or less), the formation of solid solutions for the ZrN/MoN system at U_b = -110 V appears on XRD-spectras, and for the CrN/ZrN system at U_b = -70 V.

The use of the method of modeling radiation-stimulated damage during ion irradiation has made it possible to determine the critical mixing thickness in bilayer systems. This thickness is about 4 nm for the ZrN/MoN system about 7 nm for the CrN/ZrN system.

It is established that at Λ = 20 nm the highest hardness is 44 GPa. At Λ less than 20 nm, a decrease in hardness is observed, which can be related to the formation of a solid solution in the border regions due to radiation-stimulated mixing.

FEATURES OF SYNTHESIS OF MICRO- AND NANO SIC FIBERS ON CARBON FABRIC

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In recent years, a few papers on the synthesis of SiC nanofibers on carbon fiber substrates have been published [1-2]. Such voluminous structures can be used in the development of new composites, filters and others. Thus, in [1] it is reported that the in situ growth of SiC on carbon fiber plays a decisive role in determining the oxidizing resistance of a composite. In [2], the question of the growth of SiC nanowires on the surface of flexible carbon tissue by the method of chemical vapour deposition (CVD) is considered. The results of the study have shown that SiC nanofibers grown on carbon fabric are potentially used in electronic devices and flat displays.

Taking into account the high interest in the above-mentioned studies, the authors of this work carried out research on the process of synthesis of micro and nano SiC fibers on carbon fabric by CVD method using methyltrichlorosilane (CH_3SICl_3). We used such catalysts as Fe, Co and Ni micropowders.

Experimental studies have shown that by varying the parameters of the synthesis process, coatings can be obtained both in the form of films, as well as micro- and / or nanofibers of SiC. In fig. 1 is shown CEM - image of SiC deposite on carbon fabric. As can be seen from the image, the precipitate is composed of fiber SiC.

Carbon fabric with fibrous SiC fiber can be used as a filter material for filters for fine purification of gaseous and liquid substances and as reinforcement for polymeric, metal and ceramic matrices.
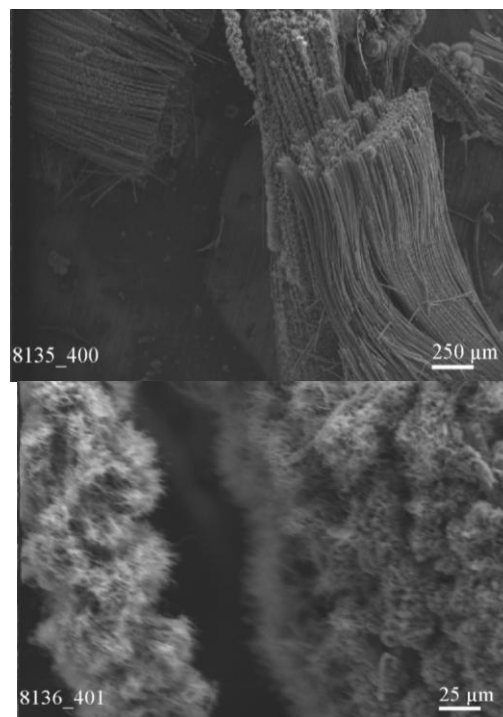
Fig. 1 - SEM - image of SiC deposite on carbon fabric

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SYNTHESIS OF NANOSTRUCTURED MATERIAL ON THE BASIS OF NANODIAMONDS MODIFIED BY SILICON

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At the present time the search for new scientific approaches and technologies that allow to reduce the sintering pressure and, as a result, the cost of nanodiamond composite materials (CM) and improve their operating parameters is the challenge in the synthesis of new diamond materials. The elimination of metal impurities catalyzing the reverse transformation of diamond into graphite makes it possible to improve the physico-mechanical characteristics of synthesized CM based on nanodiamonds significantly [1].

Silicon is traditionally used as an additive activating for diamond powders sintering: it has a good fluidity, in the molten state it reacts intensely with carbon to form a refractory carbide which has a low coefficient of thermal expansion and a high hardness [2]. The addition of silicon additives into a charge based on diamond powders leads to the formation of silicon carbide in the carbon-silicon system under HPHT treatment which will promote the sinterability of superhard materials grains at lower pressures.

The aim of the work is to obtain CM based on nanodiamonds (ND) after their vacuum annealing, modifying by silicon and sintering under various conditions (vacuum, high pressures).

The ND powder of detonation synthesis produced by Sinta Co. (Minsk, Belarus) which is purified from impurities and non-diamond forms of carbon is used as a starting material. The ND modifying is made by their annealing under vacuum conditions for the purpose of ND surface graphitizing and at the reducing atmosphere. The ND powder modifying is produced by the method of chemical-thermal treatment by means of their annealing in the temperature range 600-900°C in the presence of silicon halides [1].

As a result of vacuum sintering of the obtained composite powder ND-Si the aggregates of ND particles with sizes from 0.1 to 5 μm of different morphology with abrasive ability are obtained. In addition to diamond, in the obtained powder there is the presence of silicon carbide (α-SiC) which is formed during the interaction of silicon and carbon under vacuum sintering conditions.

As a result of HPHT treatment of the ND-Si-SiC composite powder in the pressure range of 1.0-2.5 GPa, it is obtained the material based on polycrystalline diamond grains of 0.2-0.5 μm in size, the grains consist of ND crystallites in the range of 20–100 nm. Then the synthesized compacts are mechanically milled to the powder state (fig. 1.).
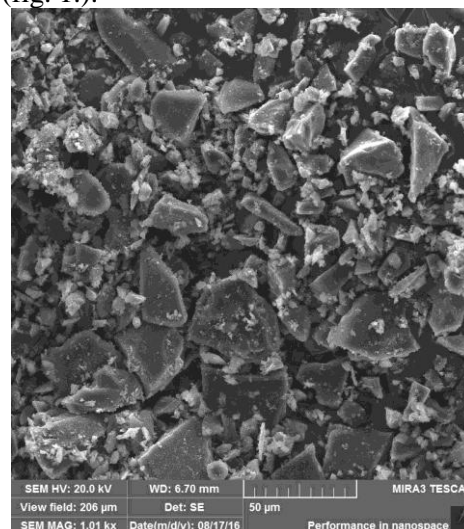
Fig.1. Diamond micron size particles on the basis of ND after Si modifying, HPHT treatment and milling

The mechanical milling of the synthesized compacts makes it possible to obtain a polycrystalline diamond micropowder with the particle size of up to 50 μm characterized by a submicron- and nanocrystalline structure.

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HEAT-RESISTANCE ALUMINOCHROME COATINGS BEING PUT ON CONSTRUCTION ALLOY BT6

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In many modern industries titanium and titanium alloys application is constantly increasing. They are used for the manufacture of containers and reactors for the chemical industry, heat transfer equipment, pipelines, pumps in the oil industry, in aircraft and automotive industries, in which high specific density and corrosion resistance play a major role. However, titanium and titanium alloys have insufficient heat- and wear resistance, which limits their practical usage as structural materials. Increasing the heat resistance and performance properties of titanium alloys can be achieved by covering them with diffusion coatings. One of the most promising ways is the formation of diffusion coatings on the surface of alloys on the basis of elements that have high chemical activity (aluminum, chromium) and form protective passivate oxide membrane that can increase the heat resistance of metals.

For aluminochrome coatings a contact powder method was used. A powder mixture which consisted of mass percentage : 28%Cr, 42%Al, 25%Al_2O_3, 5% NH_4Cl was used as the starting reagents.The saturation process was carried out in a special sealed metal chamber. The temperature of the process was 1050 ° C, time - 4 hours.

After the CTT multilayer coatings were formed on the surface of the alloy with the diffusion layers located parallel to the diffusion front with clearly defined boundaries of the section. The outer layer of Al_3Ti-based coatings had a thickness of 10.0-12.0 mcm. Intermediate layers: Al_2Ti, thickness 4.0-5.0mcm, AlTi and $AlTi_3$ - 3.0-4.5 mcm. The zone α-Ti (Al) admixed directly to the base with a thickness of 3.0-4.0 mcm. The total thickness of the coating was 26.0-30.0 mcm. In addition, the phase of Al3 (Ti, Cr) was fixed by X-rayon the outside of the coating. Its thickness doesn't exceed 4,0-5,0 mcm.

Aluminochrome samples of the alloy BT6 have a smooth gray surface. No chipping or detachment of diffusion layers is observed. Each layer of coating is separated from each other by a clear border and has its own shade. The Al_3Ti-based layer is dark gray. Each subsequent layer closer to the matrix, based on the Al_2Ti, AlTi, $AlTi_3$ and solid α-Ti (Al) compounds, is lighter than the previous one. Surface phase $Al_3(Ti,Cr)$, which is fixed by the X-ray on the surface of the coatings, doesn't differ in its microstructure from Al_3Ti. The heat resistance of the aluminum-chrome and untreated BT6 alloy was determined by changing the mass of samples in the size of $10 \times 5 \times 3.5$ mm for 1-36 hours at temperatures of isothermal exposure of 500, 700 and 900 ° C. It is established that in contrast to the untreated alloy, the oxidation of aluminochrome coatings at the temperature of 500 ° C practically doesn't occur throughout the test time: there is no increase in the mass of such specimens, whereas for an alloy without coating, the mass gain in its oxidation is: 0.0005- 0.0033 g/m^2.Excellent protective ability of coatings is maintained up to 36 hours of high-temperature tests at T = 700, 900 ° C. It has been established that the gain in the mass of aluminochrome samples is 0.0112 g/m^2, which is 26 times less compared to the increase in the mass of the untreated alloy (0.2866g/m^2).Through X-ray diffraction analysis it is that after oxidation the original coating components, Al_3Ti, Al_2Ti, AlTi, are retained, while the Al_2O_3 and Cr_2O_3phases, which are known to be heat-resistant to temperatures of 800 - 1000 ° C, are additionally fixed on the surface.

Finally, the aluminochrome coatings obtained on the surface of the BT6, because of their ability to form a dense surface membrane of Al_2O_3 and Cr_2O_3 oxides while in the air, provide its high heat resistance at temperatures of 500, 700, 900 ° C during 1-36 hours of tasting.

FORMATION OF THE STRUCTURE OF HIGH-POROUS NANOCERAMICS Al_2O_3-SiO_2

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The main problems in creating porous permeable materials are control of pore size distribution and maintaining sufficient strength at high porosity [1,2]. One of the promising materials for creating capillary-porous bodies with controlled nanopore size is the Al_2O_3-SiO_2 system.

Therefore, the aim of this work was to study the influence of technological factors on the structure formation of the high-porous Al_2O_3-SiO_2 ceramic from nanopowders alumina (α-Al_2O_3) obtained by the cryochemical method and pyrogenic silicon dioxide (grade A-175).

The highly porous nanoceramics were fabricated using the pressing and sintering operations [3].

High porosity of compacts was achieved by the selection of granulometric composition of powders and by technological methods in the manufacturing process.

Using the prepared mixture the compacts with size of Ø10x10 were prepared in a metal mold at a pressure range of 50-250 MPa.

Sintering of the samples took place in a muffle furnace in air at a temperature of 1250 ° C.

The effect of SiO_2 content in range from 20 to 50 % vol. and compacting pressure on the phase composition, microstructure, porosity, shrinkage and pore size of the oxide ceramic were investigated.

As the results of electron microscopy it is showed that after sintering of the ceramics in the investigated pressure interval (50-100 MPa) they have a biporous structure: micropores and nanopores with an average diameter of 200 nm and 30-40 nm, respectively.

An increasing in the SiO_2 nanopowder content greater than 40% vol. leads to a significant reduction in the number of nanopores, increasing in the diameter of micropores and decreasing in the total porosity of ceramics from 62 to 38%.

Presumably, the decrease in the amount of nanopores and the growth of large open pores during sintering depend significantly on the amount of introduced SiO_2 nanopowder, which is manifested in the activation of the diffusion-viscous mechanism of compaction of the ceramics.

At the same time, the increasing in the compacting pressure leads to decreasing in shrinkage and general porosity of the ceramic to 42-38%.

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NANOCRYSTALLINE AlCoFeCrVTi HIGH-ENTROPY ALLOY SYNTHESIZED BY MECHANICALL ALLOYING AND SINTERING

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High-entropy alloys (HEAs) are a fundamentally new class of materials which has been rapidly developing during the past two decades [1]. HEAs are promising candidates for many potential applications with high solid-solution strengthening, high hardness, excellent resistance to high-temperature softening, good ductility, high wear and corrosion resistance at room temperature as well as at high temperature [1 2]. High homogeneity of HEAs and nanocrystalline structure allows the improving of physical and mechanical characteristics. It can be achieved by use mechanical alloying (MA) for synthesis and next sintering under pressure at the low temperatures to maintain the initial HEAs structural state [3].

This study reports the structural evolution of AlCoFeCrVTi high-entropy alloy from elemental materials to solid solution phases during mechanical alloying, and further, to equilibrium phases during sintering under high pressure. The mechanical properties were investigated too.

The elemental Al, Co, Fe, Cr, V and Ti powders of purity greater than 99 % were mechanically alloyed using high energy planetary ball mill. The vials and balls of WC were used with gasoline as the milling medium, and the ball to powder weight ratio was taken as 10:1. MA powder was consolidated at 800°C for 30 min under the pressure of 5 GPa using High Pressure Machine type "toroid" D0044 model. To study the alloying behavior during milling, powder samples were taken at the intervals of 0.5, 1, 2, 5 and 10 h and XRD experiments were carried out in X-ray diffractometer (Ultima-IV, Rigaku) with Cu Kα radiation. Phase evolution after sintering was also studied by XRD. A SEM equipped with an energy dispersive spectrometer (EDS) was used for microstructural and composition analysis of the phases. Hardness measurements were carried out on the consolidated samples at a load of 1 N using a conventional microhardness machine equipped by standard Vickers pyramid.

XRD pattern reveals the phase formation in AlCoFeCrVTi HEA with milling time. From the XRD results it is clear that the alloy formation is completed after 10 h with the formation of BCC solid solution with a lattice parameter of 0.2904 nm and the crystallite size is about 15 nm. A small volume fraction of tungsten carbide was observed as the result of milling by MA. Thus, nanocrystalline single phase solid solution of a simple structure such as BCC could be synthesized in this equiatomic alloy by MA.

The XRD pattern of the MA powder consolidated under pressure at 800°C confirms that the BCC solid-solution is metastable. After sintering the AlCoFeCrVTi HEA is composed of two solid solutions with FCC and BCC structure and the small volume fraction of tungsten carbide. The phase with the FCC structure is dominant with a content about 60 % by weight. The lattice parameter of the phases present in the alloy are 0.3597 nm (FCC) 0.2882 nm (BCC), respectively. After sintering under pressure, the AlCoFeCrVTi alloy remains in a nanocrystalline state with a crystallite size about 50 nm, and the porosity of the sample doesn't exceed 1 vol. %. According to the experimental results the AlCoFeCrVTi alloy has a Vickers microhardness of 13.9±0.4 GPa. The high hardness is ascribed to the solid solution and nanocrystalline strengthening effect.

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STRUCTURE, MECHANICAL CHARACTERISTICS AND STABILITY OF (Ti,Nb)-Al-C MAX-PHASES-BASED COMPOSITES IN HYDROGEN AND OXIDIZING ATMOSPHERE

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The developed materials are promising for interconnects of hydrogen fuel cells, damping material in machine building, in nuclear industry, for pantographs or sliding bearings, etc. The dense MAX-phases-based materials of Ti,Nb–Al–C systems prepared by hot pressing at 30 MPa are stable in hydrogen and oxidizing environments at 600 °C, are about twice lighter (ρ = 4.27 g/cm3) and more stable in air (for 1000 h) than Cr-containing "Crofer" steels. The addition of Nb leads to the formation of about 10 times thinner surface oxidized layer and thus to the material stability increase. The most resistant among the studied materials in air at 600 °C for 1000 h turned out to be Ti_2AlC-based (73 wt.% of Ti_2AlC according to Rietveld refinement). The SEM study of it matrix revealed the near $Ti_{2,3}AlCO_{0,2}$ composition and the presence of elongated near $Ti_{3,6}AlC_{1.9}O_{0,6}$ grains. Somewhat less stable was preliminarily oxidized at 1200 oC (for 2 h) Ti_3AlC_2 (89 wt%). The Ti_3AlC_2-based materials at room temperature demonstrated 4.6–5.8 GPa microhardness at 5 N load, 500–570 MPa bending and 700–1300 MPa compression strengths, 10.2±0.4 MPa·√m fracture toughness and 2.7·106 S/m electrical conductivity at 20 °C. The bending strength of Ti_3AlC_2-based material in air at 20 °C was 535 MPa, after keeping at 600 °C in air and hydrogen it decreased to 490 and 500 MPa, respectively. For $(Ti,Nb)_3AlC_2$ –based materials the bending strength at 20 °C in air was 480 MPa and increased by 10% after heating at 600 °C both in air and in hydrogen. The estimated damping coefficient and stability to radiation of the MAX-phases were as well high.

STRUCTURE FORMATION DURING SYNTHESIS OF TITANIUM DIOXIDE UNDER PILOT INDUSTRIAL CONDITIONS

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For the development of the manufacturing technology of titanium dioxide nanopowders of anatase modification, a laboratory technology for preparing TiO_2 was developed.

A study of the evolution of the porous structure of intermediate decomposition products of titanium hydroxide under nonisothermal conditions formed the basis for choosing a laboratory technology for the synthesis of TiO_2 anatase powders for the adaptation to the conditions of a pilot industrial technology.

In the present work, structure formation in the process of preparation of TiO_2 in different regimes was investigated. For the synthesis of TiO_2 powders of anatase modification, $TiO(OH)_2$ semiproduct (manufactured at the Sumy chemical plant) washed from iron sulfate was used. To improve the technological properties, the semiproduct powder was granulated with a 3% solution of polyvinyl alcohol with subsequent sieving through a screen and drying.

Nanopowders were investigated by the methods of XRD, IR spectroscopy, transmission electron microscopy (TEM), and adsorption-structural analysis.

Properties of the obtained nanodisperse TiO_2 powder coincide with properties of TiO_2 powder synthesized under laboratory conditions.

According to the XRD data, TiO_2 obtained in the semi-industrial rotational synthesis furnace has the modification of anatase of the tetragonal crystal system with lattice constants $a = 3.784(1)$ Å and $c = 9.493(7)$ Å (Fig. 1).
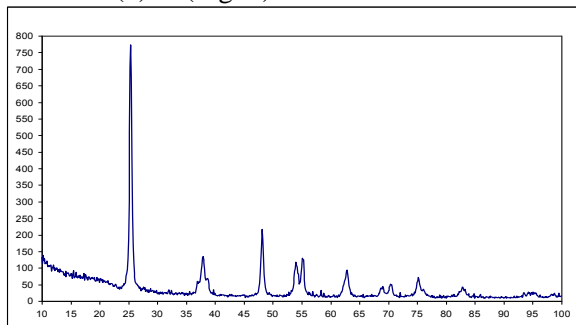
Figure 1 – X-ray diffraction pattern of TiO_2 obtained in a semi-industrial rotational synthesis furnace

According to the TEM data, the obtained TiO_2 powder of anatase modification is rather aggregated, but aggregates are soft and have a size from 50 nm up to 500 nm. Powder particles are practically monodisperse and have a size of ~10 nm (Fig. 2).
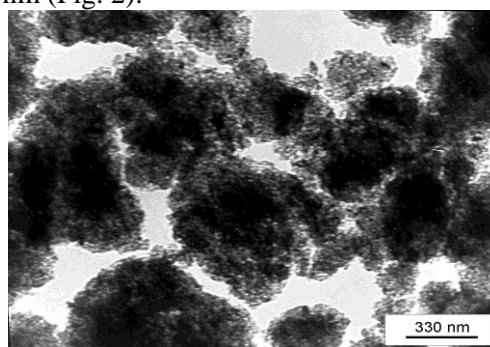
Figure 2 – TEM image of particles of TiO_2 powder obtained by the pilot-commercial technology

According to the results of the adsorption-structural analysis, the main criterion of completion of the TiO_2 synthesis process is the disappearance of nitrogen sorption isotherms. The second criterion is the particle size calculated from the values of the specific surface area. The obtained powders belong to nanodisperse mesoporous systems of predominantly layered structure and have a specific surface area of 60–70 m^2/g. The particle diameter calculated from the values of the specific surface area ranges from 20 to 25 nm, and the average pore diameter ranges from 10 to 12 nm.

Conclusions

1. Under conditions of pilot industrial technology, powders of titanium dioxide of anatase modification with lattice constants $a = 3.784(1)$ Å and $c=9.493(7)$ Å and with a particle size of ~10 nm were obtained.

2. According to the data of the adsorption-structural method, the synthesized powders belong to nanodisperse mesoporous systems of predominantly layered structure with a specific surface area of 60–70 m^2/g and an average pore diameter ranging of 10–12 nm.

AlNiCoFeCrTiB$_x$ HIGH-ENTROPY ALLOY COATINGS REZULRED FROM ELECTRON BEAM WELDING

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In many situations, only the contact surface properties are important in determining performance of the component in practical applications. Therefore, the use of a coating from materials with high physical and mechanical characteristics, such as high-entropy alloys (HEA) [1], has several attractive advantages. HEAs have been found to have novel microstructures and unique properties. At the same time, by controlling the composition of HEA, it is possible to achieve high hardness, wear resistance, corrosion resistance, oxidation resistance, high temperature performance [1]. Nowadays the primary method to synthesize HEAs is vacuum arc remelting for bulk cast ingot, surface coating and mechanical alloying is also possible [1, 2]. Considering HEA's tendency to form simple structures, fabricating HEA coating by electron beam welding process is of great significance and potential for extensive use. Until now this novel method for preparing HEA coatings has just been reported by any organizations.

The purpose of this work is to study the features of microstructure, phase and chemical composition, and microhardness of HEA coatings, produced by electron-beam welding on steel substrate of 6 and 7-component powder equiatomic mixtures of the system Al-Ni-Co-Fe-Cr-Ti-B$_X$. In order to evaluate the influence of B content in AlNiCoFeCrTiB$_X$, the x factor was set as variable quantity and the experiments were divided into 4 groups: x=0, 0.25, 0.5, and 1.0. All the elements except B are equiatomic. The microstructure, chemical composition, and constituent phases of the synthesized coatings were characterized by SEM, EDX, and X-ray diffraction (XRD) analysis. Microhardness HV was also evaluated.

Experimental results demonstrate that the AlNiCoFeCrTiB$_{0-0.5}$ HEA coatings are composed of only two substitutional solid solutions with body-centered cubic (BCC) structure (Fig. 1) and different lattice parameter due to different component concentration. The coatings exhibit dendritic microstructure with different size and morphology. With the increase in the boron content to x = 1, the phase composition changes and in the AlNiCoFeCrTiB coating formation of

one bcc solid solution and Cr$_2$B TiB$_2$; and BCr$_{0.2}$Fe$_{1.8}$ borides is observed; due to the presence of excess boron atoms, do not dissolve in the void spaces of the bcc crystal lattice of the substitutional solid solution.
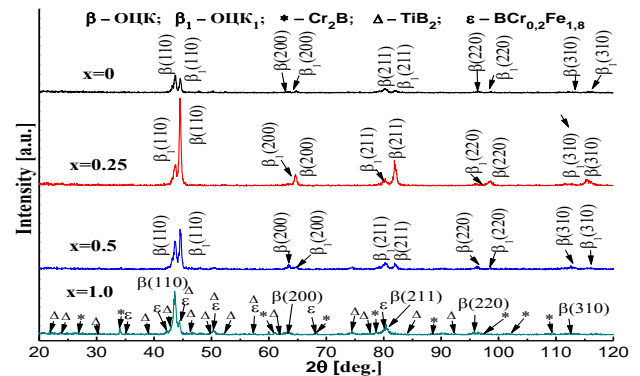
Fig. 1. XRD patterns of AlNiCoFeCrTiB$_x$ HEA coatings resulted from electron beam welding

The addition of boron (0,25; 0,5; 1) to original mixture AlNiCoFeCrTi leads to distortion of the crystal lattice and increase in hardness from 8,7 GPa to 12.8 GPa and then with a maximum content in AlNiCoFeCrTiB coating due to appearance of borides to 14,2 GPa.
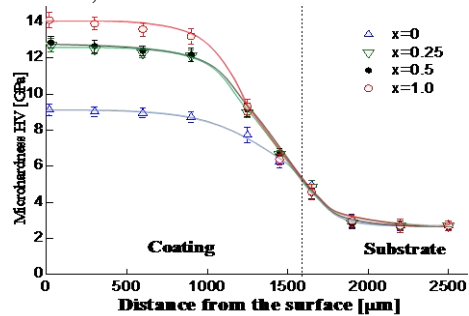
Fig. 2. Hardness of AlNiCoFeCrTiB$_x$ HEA coatings resulted from electron beam welding

The hardness of high entropy AlNiCoFeCrTiB$_X$ coatings is much higher than that of the initial components and than the one of the steel substrate, and is much higher than that of the similar alloys prepared by laser cladding technique.

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DETERMINATION OF ENERGY OF ACTIVATION OF OXIDATION OF FREE-CARBON IN INDUSTRIAL POWDER OF CARBIDE BORON

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Boron carbide (CB) is one of the few materials with a wide range of applications. High melting point, thermal stability, hardness, low density, neutron absorption ability (carbide enriched with boron isotope ^{10}B), as well as semiconductor properties at high temperature are combined into a unique combination characteristic for this compound. Industrial powders of boron carbide, as a rule, are a mixture of polytypes. The polytypes are stable when the carbon content is above 8 and below 20 atomic percent.

The purpose of the present work was to study the temperature, kinetic (activation and velocity) characteristics of the total oxidation of the constituents of the phase of CB (C_{CB}) and free carbon (C_{free}) ($C + O_2 \rightarrow CO_2$).

Energy-activation characteristics of CB oxidation reactions were calculated using the Svante Arrhenius method [1, 2]. The results obtained are presented in Table 1. As can be seen from the data presented, $E_{act} C_{free}$ is equal to 174,1 and 178,9 kJ / mol in the region of 973 - 1173 K, and for C_{CB}: 29.2 and 40.8 kJ / mol at 1073-1473 K, respectively.

Table. 1. Energy activation rates of oxidation reactions of free carbon and constituents: carbon and boron-phase CB.

T (K)	E_{act}, v_{ox} kJ/ mol			
	C_{free}		C_{CB}	
	№1	№2	№1	№2
973-1173	174,1	178,9		
1073 - 1473			29,2	40,8

In the temperature range 973 - 1473 K, the rate of oxidation of free carbon at the attainment of 1173 K stabilizes and amounts to $(2.61 \pm 0.10) \cdot 10^{-5}$ mol·s^{-1} ta $(3.78 \pm 0.30) \cdot 10^{-5}$ mol·s^{-1}, respectively.

The oxidation rates of carbon in the CB phase are the lowest. In the studied temperature range they range from $(4.58 - 3.89) \cdot 10^{-7}$ mol·s^{-1} at 973 K to $(1.94 - 1.81) \cdot 10^{-7}$ mol·s^{-1} at 1073 [3].

The possibility of direct measurement of impurities of nanoforms of free carbon in powders of industrial boron carbide is realized. The method makes it possible to quantitatively determine the impurities of nanotubes, nanorublets, transverse, cone and folded-layer carbon nanofibers, etc. with a detection limit of up to 0.25-0.10% with a relative error not worse than σrelate ~ 5.0 to 3.0 %. At the same time, the temperature resolution makes it possible to reliably separate many nanoforms of carbon with similar characteristic temperatures (for example: rolled-layer fibers (t_{ox}-740 ° C), many wall nanotubes (t_{ox}-760 ° C) of two walled (t_{ox}-780 ° C) and one walled nanotubes (t_{ox}-800 ° C).

This technique significantly expands the arsenal of existing instrumental capabilities. Unlike the known methods, the proposed method provides reliable, averaged over a large sample volume with sensitivity, which meets the needs of modern technologies. The technique can be used as the basis for the certification procedure for carbon nanomaterials in the ISO standard format.

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STRUCTURAL - PHASE TRANSFORMATIONS IN FORMING POWDER PARTICLES OF THE REFRACTORY COMPOUNDS RECEIVED BY CARBOTHERMAL SYNTHESIS

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In this paper, a generalization of data on the study of methods of translucent electron microscopy and X-ray diffraction analysis of structural and phase transformations is presented, which is carried out with increasing temperature of carbothermal synthesis of some representatives of nitrides, carbides, and borides (BN, AlN, Si_3N_4, SiC, B_4C, TiB_2). A common feature of the conditions for the synthesis of these compounds was the use as a starting component of sucrose (as a source of active reducing agent – nanodispersible carbon).

The generalization is based on the results of research on powder samples (as model objects) created during the development of technologies for obtaining these compounds by employees of IPMs NASU, belonging to G.Samsonov's school *.

The general patterns of structure formation during synthesis of the investigated compounds are revealed. They are determined by the development of the following structural transformations.

- At the initial stage (for these compounds temperature is not more than 1300^0C), the synthesis of compounds takes place, with the formation of nanodispersed particles on their basis (the range of sizes for monocrystalline particles is 20-100 nm). On the basis of particles, aggregates of different densities and sizes are formed.

- The integration of particles promoting loosening of units.

- Appearance of substructure in particles: packing defects in cubic (3C) SiC, polysynthetic twin crystals in (3C) SiC and B_4C, microdomain substructure in 6H SiC.

- Phase (3C 6H) and polytypical (6N multilayer polytypes) transitions in silicon carbide and phase transformation into silicon nitride .

- Further aggregation of particles, the emergence of bridges between them and the appearance of flat elements of particle cutting, as well as the particles of the correct cut in general.

- Synthesis of these compounds due to the development of gas-phase reactions. In this case, the growth of particles of an anisometric shape takes place (these are needles, fibers, filaments, thin plates with a form factor that reaches 10 units or more).

- Free sintering of powder particles with the formation of boundaries of intergranular type (collectively recrystallization).

For boron nitride, a number of special structural transformations have been identified during synthesis. This is the formation of nanoparticles in the form of anions of various crystallogeometry and their combinations both in the solid phase at the low-temperature stage of synthesis and in the conditions of the development of gas-phase reactions. In the latter case, there is also the formation of nanotubes of different sizes (in cross section and length) with a distinct phase composition and crystallomorphology. Tubes of cylindrical section, as a rule, are composed by a graphite-like hexagonal phase BNg, facetted ones - by a rhombohedral phase BNr. At the high-temperature synthesis stage, the destruction of tubes of both types occurs, and a crystal-oriented phase transformation of BNr - BNg takes place.

In general, this method of carbothermal synthesis with the use of highly active carbon, depending on the temperature of the process, makes it possible to obtain powders of various dimensions (from the dimensions of single crystals not more than 100 nm and up to tens of microns), with a different substructure in the particles, different crystal morphology of particles and phase composition.

LIGHT-EMITTING PROPERTIES OF DIFFERENT BORON NITRIDE POWDERS

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Boron nitride (BN) is an attractive material due to its unique mechanical and thermal properties, low density, electrical insulation, inertness, etc. Among the applications, much less attention was paid to light-emitting properties of BN powders. The studies of BN photoluminescence are scarce, and the processes leading to light emission in BN powders are far from beingcompletely understood. Therefore, the aim of the present study was to investigate light-emitting properties of different BN powders morphologiesfabricated by different processings.

We studied (Fig. 1) the samples of turbostratic(1) andpyrolitic(6) BN, powder ofChempur Company (7)and fourBN powdersobtained catalyst-free synthesis under concentrated lightin axenon high-fluxoptical furnace in flow of nitrogen. Four BN powders were fabricated by heating of: a – initial BN powder ofChempur Company (2); b - amorphous boron powder with mean particle size of 0,05 μm (3); c - boron powder with carbon impurities of mean grain size of 0,20 μm (4); d - boron powder of Merk company with mean grain size of 2,00 μm(5) (**Fig. 1**).

Structure, morphology and phase composition of all materialsunder study werecharacterized by scanning electron microscopy (SEM) andpowder X-ray diffraction (XRD. Optical properties of BN were presented by photoluminescence (PL) method under band-to-band excitation conditionsand excitation via defect-related levels at room temperature.

It was demonstrated an effect of structure, morphology and phase composition on light-emitting properties.

Results of the photoluminescence studies of BN samples obtained by different synthesis procedures are shown in **Fig.1**. It is seen that the efficiency of light emission strongly depends on the procedure of BN nanoparticles growth. The highest intensities of emission are observed for turbostratic and pyrolitic BN, while the nano-BN powders obtained by the catalyst-free synthesis in the optical furnace are much less efficient light-emitting materials.
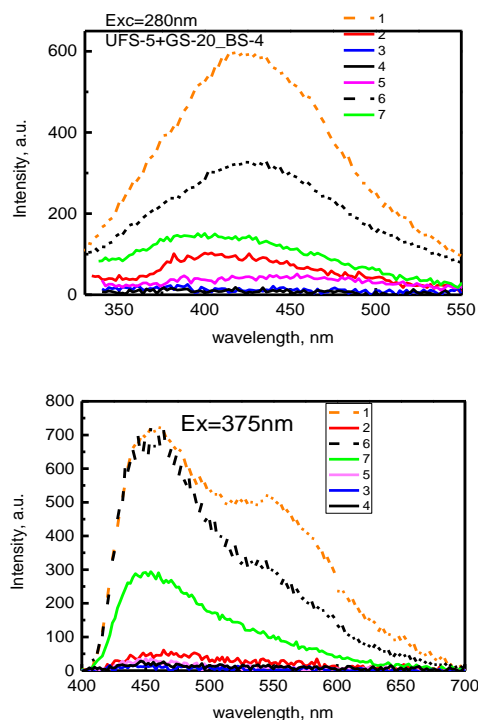
Fig.1. Photoluminescence spectra of different BNpowders described in the textin detail.The spectrawere measured at 280 nm (a) and 375 nm (b) excitation.

It was shown that at the excitation with λ_{exc} = 280 nm all types of BN nanoparticles demonstrate rather wide luminescence band in the visible spectral range with the maxima positions varying from 400 nm to 425 nm. At the excitation with λ_{exc} = 375 nm only the low-energy wing of this band is observed in all spectra; moreover, in the spectra of two types of samples – turbostratic and pyrolitic BN – an additional band with the maximum at ˜550 nm appears.

EFFEKT OF MODIFICATION METHODS ON PHYSICAL AND CHEMICAL CHARACTERISTICS OF SYNTHETIC DIAMOND NANOPOWERS

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The wear resistance of the abrasive tool is largely dependent on the bond strength of the diamond-binder. This becomes particularly important if the binder is made on the basis of refractory compounds.

The adsorption activity and the increased specific surface area of the powder contribute to the formation of bonds between the diamond particles and the binder.

The aim of this work is to study the influence of methods of liquid-phase modification of nanopowders of synthetic diamond on the formation of their physicochemical characteristics.

DSUD 99 nano-powders of diamond were examined before and after the modification. The powder was modified by thermochemical aging in a mixture of chromic and sulfuric acids, a mixture of nitric and sulfuric acids of acids, as well as in an alkaline melt and normalization of the surface with distilled water at the boiling point.

The adsorption-structural and physicochemical characteristics of diamond nanopowders were determined by nitrogen adsorption at low temperatures using the NOVA 2200 gas-adsorption analyzer (Quantachrome, USA). The energy state of the surface was estimated from the adsorption and specific adsorption potential and surface energy. The uniformity of the powders was determined using a system-criterial method for quantitatively estimating the homogeneity of dispersed SHM. The specific magnetic susceptibility, the resistivity, the mass fraction of the impurities were determined by the methods developed in N. Bakul Institute for Superhard Materials National Academy of Sciences of Ukraine.

According to the results of the research it is established that due to liquid-phase modification of the initial nanopowder the following indices decrease: the content of impurities is 1,5–2,0 times, the specific magnetic susceptibility is 2,2–3,2 times; the specific electric resistance increases by 1–2 orders of magnitude, the specific surface area by 12–20%, the pore volume by 4,0–12,0%, the average pore radius by 5,0–9,0%, the adsorption potential – by 68%, specific adsorption potential – by 53%.

Powders after modification have a micro-mesoporous structure with developed mesoporosity.

As a result of the thermochemical excitation of the powder in an acidic medium, the free surface energy is 802 to 805 J/g, in an alkaline medium – 729 J/g.

Modification of the powder surface leads to a heterogeneous distribution of the adsorption potential. The homogeneity index of the adsorption and specific adsorption potential distribution is 0.50–0.54. The specific adsorption potential increases from 0.78 to 3.13 J/m 2 after the thermochemical vigil to the acid medium, from 0.78 to 2 in the alkaline medium, 76 J/m^2.

The use of different methods of liquid-phase modification of the original ASDU-99 diamond nanopowder makes it possible to influence the formation of their physico-chemical and adsorption-structural characteristics, it makes it possible to increase the values of the adsorption activity and specific surface area, and also the homogeneity of the adsorption and specific adsorption potentials distribution.

EFFECT OF TEMPERATURE ON THE CONSOLIDATION OF NANOCRYSTALLINE POWDERS IN THE ZRO$_2$-Y$_2$O$_3$-CEO$_2$ SYSTEM

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Microstructural design of ZrO$_2$-based materials for medicine in the ZrO$_2$-Y$_2$O$_3$-CeO$_2$ system includes three basic principles: using costabilized with Y$_2$O$_3$ and CeO$_2$ ZrO$_2$ nanocrystalline powders; creating regular samples microstructure from these powders; sintering of samples at lowered temperature ($\approx$ 1300 °C), which provides the materials with fine-grained microstructure.

The starting powder high specific surface area preservation as a factor of maintaining its activity is necessary, but not sufficient, to achieve the required strength behavior of sintered ceramics. The ceramics properties are determined by the set of starting powders' properties, as well as by the features of their consolidation.

Object of investigation: to find the effect of thermal treatment temperature of the starting powders in the ZrO$_2$–Y$_2$O$_3$–CeO$_2$ system on their consolidation.

The starting powders were produced by the hydrothermal method in an alkaline medium. The obtained powders were thermally treated in the 400–1300 °C range. Powders with the compositions (mol%): 90ZrO$_2$–2Y$_2$O$_3$–8CeO$_2$ (1); 97ZrO$_2$–3Y$_2$O$_3$ (2); 88ZrO$_2$–12CeO$_2$ (3) were used for the investigation. Green bodies (d=20 mm) were formed from powders 1-3 using a cold uniaxial pressing.

The variation of the relative compacts density depending on the powders' processing temperature is shown in Fig. 1 and the sintered at 1300 ^{o}C samples in Fig. 2.

Formable powders are complex systems in their structure, since they consist of agglomerates of the first and second orders, the strength of which increases with increasing heat treatment temperature. In addition, during the treatment, the phase transformation F-ZrO$_2$→T-ZrO$_2$ and sintering of powders occurs.

The behavior of the plots shown in Fig. 2 are determined by the phase composition of the samples, the agglomerates strength behavior of the starting powders, and the effect of "zonal isolation".
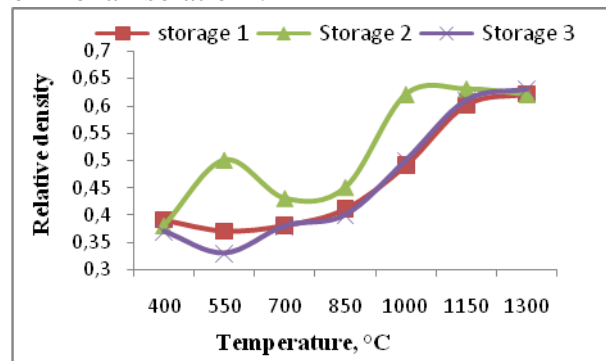
Figure 1 – The relative density variation of the green bodies depend on the temperature of the thermal treatment of the starting powders in the ZrO$_2$-Y$_2$O$_3$-CeO$_2$ system.
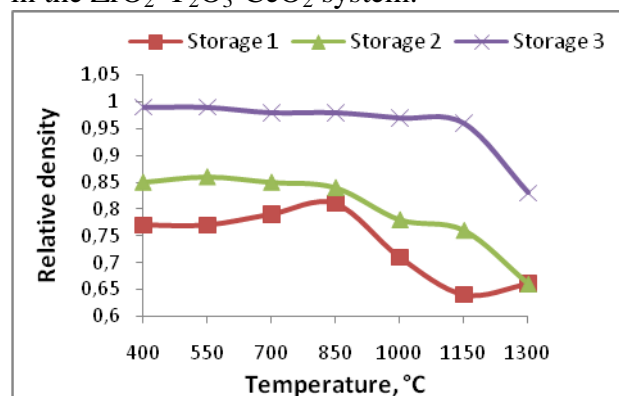
Figure 2 – The relative density variation of sintered ceramics depend on the temperature of the thermal treatment of the starting powders in the ZrO$_2$-Y$_2$O$_3$-CeO$_2$ system.

Thus, for the formation of ceramics regular microstructure, complex treatment of the starting hydrothermal nanocrystalline powders in the ZrO$_2$-Y$_2$O$_3$-CeO$_2$ system is necessary to restrict the effect of the "topochemical memory" on the ceramics' properties.

УКРАИНСКАЯ НАЦИОНАЛЬНАЯ ТЕХНОЛОГИЧЕСКАЯ ПЛАТФОРМА (УНТП) «НОВЫЕ МАТЕРИАЛЫ И ТЕХНОЛОГИИ ИХ ИСПОЛЬЗОВАНИЯ» КАК ИНСРМЕНТ УСКОРЕННОГО ТРАНСФЕРА НАУЧНЫХ РАЗРАБОТОК В ПРОМЫШЛЕННОСТЬ

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Целью создания технологических платформ является :

- реализация коммуникационного механизма на уровне государственно-частного партнерства для обеспечения научно-технологического и инновационного развития экономики Украины, создание эффективного научного пространства;
- практическая реализация результатов научных исследований как предприятиями малого бизнеса, так и промышленностью в целом;
- объединение промышленных предприятий и организаций научно-исследовательского сектора для удовлетворения потребностей промышленности Украины в новых материалах и технологиях их изготовления.

Деятельность УНТП будет направлена на:

- разработку стратегии развития исследований для потребностей отечественной промышленности, организации банка разработок «Новые материалы»;
- решение вопросов трансфера научных разработок в промышленное производство;
- установление научных, коммерческих и производственных отношений с зарубежными партнерами для участия в европейских двусторонних и многосторонних программах;
- решение правовых вопросов;
- поиск инвесторов всех форм собственности;
- создание предприятий, пилотных участков, стартапов и т.п.;
- подготовка специалистов в области маркетинговой деятельности.

Координация УНТП будет осуществляться по таким научным направлениям:

- новые металлические материалы и покрытия;
- передовая керамика (металлоподобные тугоплавкие соединения);
- твердые сплавы и алмазосодержащие материалы;
- композиты (на основе металлов, керамики, полимеров);
- современные полимерные материалы;
- углеродные материалы (фуллерены, графены, нанотрубки).

Институтами НАН Украины подготовлен первый вариант перечня инвестиционных проектов для УНТП. Он содержит около 50 проектов, имеющих важное значение для экономики Украины и относящихся к приоритетным направлениям – охране здоровья, жизнеобеспечению людей, охране окружающей среды, энергетике, транспорту.

HIGH-TEMPERATURE IN-SITU COMPOSITES BASED ON MULTI COMPONENT TITANIUM MATRIX REINFORCED BY SILISIDO-BORIDE

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As shown by us earlier [1], strength and hardness of a superfine ternary eutectic $(Ti) + Ti_6Si_2B + (Ti_5Si_3)$ alloy (the reinforcing phase is mainly of Ti_6Si_2B of ~200 nm section) are higher than those for binary titanium-boride and titanium-silicide ones. The high level of compressive yield strength about 470 MPa of the ternary alloys was found to retain up to 700°C. The aim of the present work is to increase the high-temperature strength characteristics of hypo-eutectic and eutectic $(Ti) + Ti_6Si_2B + (Ti_5Si_3)$ alloys by alloying with Al, Sn and Zr, as well as by high-temperature deformation.

Six 4-5 kg alloy ingots obtained by electron-beam crucible-skull melting (EBSM) have been investigated. The regimes of melting allowed producing the homogenous ingots, by compositions and by structure (as followed from the data of structure examinations and mechanical testing). The alloys under study were eutectic Ti-9.6Si-3.7B (at.%) [phases (Ti) and Ti_6Si_2B were identified]; hypoeutectic Ti-8.2Si-3.0B $[(Ti) + (Ti_6Si_2B)$ with negligible amount of boride TiB], Ti-0.7Zr-5.1Al-0.3Sn-8.0Si-3.9B, Ti-0.3Zr-0.5Al-2.9Sn-9.5Si-2.3B, and Ti-1.2Zr-5.5Al-2.1Sn-8.7Si-2.5B (at.%). The alloy Ti-0.7Zr-5.5Al-3.6Sn-8.4Si-2.5B (at.%) demonstrated conglomerate three-phase $(Ti) + (TiB) + (Ti_5Si_3)$ structure. The most disperse eutectic constituents were found in the hypoeutectic Ti-1.2Zr-5.5Al-2.1Sn-8.7Si-2.5B (at.%) alloy.

The EBSM as-cast hypoeutectic ternary three-phase alloy Ti-8.2Si-3.0B (at.%) exhibits high strength characteristics at room and high temperatures (σ_{02} ~960 MPa at ambient temperature and 349 MPa at 700°C), along with ambient-temperature plasticity and fracture toughness of ~0.5 % and 11 MPa·m$^{0.5}$.

Alloying with tin and aluminium (~5 and ~3 at.%, respectively) increases the strength at room temperature by ~100 MPa, but reduces microplasticity by an order of magnitude as compared to these characteristics of the ternary alloy. The high strength of six-component as-cast alloys (which could be expected on the basis of hardness tests) was not achieved owing to their absolute brittleness at room temperature.

So, all of the alloys studied exhibit low plasticity in as-cast state. As shown high-temperature deformation (forging of peaces heated to 1050°C in air) leads to increasing plasticity of the hypoeutectic ternary Ti-8.2Si-3.0B (ат. %) alloy by a factor of 4-6 (to 2-3 %) and fracture toughness by a factor of 3 (to 36 MPa m$^{0.5}$) with remaining high level of high-temperature strength (317 MPa at 700°C).

After high-temperature deformation, micro-plasticity of quaternary alloys increases by an order of magnitude (to 0.2-0.3 %) and fracture toughness by 40 % (to 20 MPa m$^{0.5}$). After deformation the absolutely brittle Ti-1.2Zr-5.5Al-2.1Sn-8.7Si-2.5B (at.%) alloy exhibits plasticity of 0.02-0.05 % and doubles fracture toughness (to 26 MPa m$^{0.5}$) as compared to these characteristics of the as-cast materials. Its high-temperature strength equals 887 MPa at 700°C, that is three times higher that of the wrought ternary alloy.

Thus, after forging the six-component titanium based alloy (Ti-Zr-Al-Sn-Si-B), reinforced mainly with the silicide-boride phase Ti_6Si_2B, possesses high elevated-temperature strength, 887 and 572 MPa at 700 and 800 °C respectively, which almost doubles this characteristic of the titanium alloy Ti-1Mo-1Nb-5.5Zr-6Al-2.5Sn-6Si (wt.%), one of the most high-temperature-resistant titanium alloys (330 MPa at 800°C), and is almost three times higher than its previous analog, namely the titanium-based Ti-Zr-Al-Si alloy TIKAD reinforced with silicide (Mazur V.I. et al. USA pat., 1994, 1997).

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BRAZED METAL-QUARTZ SCINTILLATION CHAMBERS FOR WORKING IN EXTREME CONDITIONS

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Brazed metal-quartz products are widely used in modern technique. They are used in cryogenics, microwave technology, electronics, space technology and many other industries. One of the important and promising areas is the creation of brazed quartz-aluminum scintillation chambers used in geological equipment, mainly using the gamma-ray logging method. Such chambers should be operated under extreme conditions, including simultaneous impact of abrupt temperature changes from -50 °C to +250 °C (up to 1000 thermal cycles), mechanical action and shock loads while maintaining high chamber tightness and no stresses in the optical element made of quartz glass.

Technological modes of brazing, including preliminary metallization of the aluminum frame and brazing of the quartz-aluminum chamber at 620 °C for one hour are developed.

In this study, as a result of the wetting with lead-based plastic solders with additions of tin, indium, silver and copper of aluminum alloys A-995, AD1, AMn an indium-lead composition as solder was selected for brazing an optical element made from quartz glass to the chamber of an AMn alloy. Such a ductile alloy is the most optimal for brazing materials that are very different because of temperature coefficients of linear expansion (α) of materials, such as quartz glass ($\alpha = 5 \times 10^{-7}$ 1/K) and aluminum alloys ($\alpha = 22 \times 10^{-6}$ 1/K for aluminum), from the viewpoint of minimizing residual mechanical stresses in the optical element of the chamber.

Two types of scintillation chamber design have been developed: the end seal and the surrounding seal.

Experienced samples of brazed quartz-aluminum scintillation chambers were produced and tested (fig. 1). These samples were capable withstand without disturbing the vacuum density of the chamber, and in the absence of mechanical stresses in quartz optical element, the action of 1000 thermocycles in the -50 °C ÷ +250 ° C mode with simultaneous vibration and shock loads including mechanical single shocks with an acceleration of 100g with a duration of impact of 11 ms; number of impacts is three in two mutually perpendicular directions (x and z).

Fig.1. Brazed quartz–aluminum (AMn) samples.

RESEARCH OF PHASE COMPOSITION AND PROPERTIES OF POWDER CARBIDE STEEL OBTAINED WITH USE OF WASTE SHKH15

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The properties of carbide steels depend to a large extent on the properties of the refractory and metallic constituents. At the same time, when using the traditional technology for the production of a carbide steel including grinding of a charge consisting of titanium carbide powders and an iron-based alloy, pressing the blanks and liquid-phase sintering at 1350 ° C, one does not fully realize their positive properties due to the incomplete wettability of the particles titanium carbide with a steel binder.

A new approach was proposed, which consists in the fact that the carbide phase is formed during the reaction sintering of powder mixtures consisting of titanium, steel and carbon powders at 1300 ° C.

The paper presents the results of the study of the formation of the phase composition in the impregnation process with mixtures of 3% $MnSi_{1.77}$-97% Cu and 5% $MnSi_{1.77}$-95% Cu powder carbide steels of composition (40% Fe-60% TiC) obtained using slurry wastes of steel ShKh15.

When carbide steels are impregnated with a copper compound containing 3% and 5% manganese silicide, copper is the main phase.

In both composites, there are carbide phases of TiC and SiC. The predominant carbide phase is the TiC phase.

Copper in the structure of the composite is distributed in the form of a broken mesh along the grain boundaries.

It is shown that a material containing 3% manganese silicide in the impregnating mixture differs from the material using an impregnating mixture with 5% manganese silicide, phase composition, structure and hardness.

A characteristic feature of the composite obtained by impregnating the mixture containing 3% manganese silicide is the formation of the iron silicide Fe_5Si_3 phase. Composites have a finer-grained structure and a higher microhardness of 12.36 GPa, since the base of the composite is a solid solution based on copper. Microhardness of the composite obtained by impregnating with a mixture of 5% manganese silicide 8.45 GPa. In the X-ray spectrum of the alloy obtained using an impregnating mixture with 5% manganese silicide, copper is fixed by two structures of the fcc lattice - one structure belongs to non-alloyed copper, the other structure of the HCC belongs to the copper alloy.

Thus, the presence on the surface of the sample of the predominant more plastic phase on the basis of copper and hardening carbide phases can be prerequisites for combining the strength and plastic properties of composites.

a)   b)
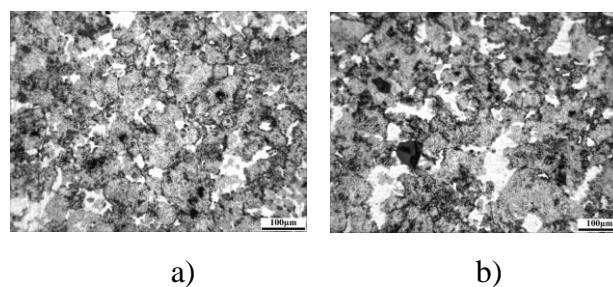
Figure 1. Microstructure of composites (40% Fe-60% TiC) after impregnation with 3% $MnSi_{1.77}$-97% Cu (a) and 5% $MnSi_{1.77}$-95% Cu (b) mixtures.

I

IV

X