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VI International Conference

"Fundamental Bases of Mechanochemical Technologies"

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BOOK OF ABSTRACTS

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Preface

Welcome to the FBMT 2022! The VI International Conference "Fundamental Bases of Mechanochemical Technologies" (FBMT 2022) will be held on November 21-24, 2022 in Novosibirsk, Russia. It is hosted by the Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences.

The Institute of Solid State Chemistry and Mechanochemistry SB RAS has made a significant contribution to the development of new technologies based on mechanochemical reactions and mechanical alloying. The I International Conference on Fundamental Bases of Mechanochemical Technologies organized by the Institute was held in 2001 in Novosibirsk; the II Conference was jointed with the VIII International Conference on Sintering and was held in Novosibirsk in 2004. The III Conference in this series was organized by the Institute and held in 2009 in Novosibirsk. The IV FBMT was held in Novosibirsk in 2013. Year after year, the Conference had demonstrated a growing interest from research organizations and industries to the mechanochemical technologies. The participation of Chinese organizations, Science and Technology Society of Guangdong Province and Dalian Jiaotong University, in the organization of this Conference guarantees active participation of foreign scientists in the Conference. The Conference has attracted a total of 155 contributions; 100 are scheduled for oral presentation. The contributions were submitted by scientists from 10 countries throughout the world.

The present Book of Abstracts introduces recent advances in mechanical alloying, mechanochemical synthesis and production of new materials by the mechanochemical methods.

We thank our sponsors for the financial support of FBMT 2022:

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Without their help, it would have been impossible to prepare this event successfully.

We hope that the Conference will stimulate new research activities and help establish and strengthen international cooperation.

N. Z. Lyakhov
Chairman of FBMT 2022

SCOPE OF THE CONFERENCE

VI International Conference "Fundamental Bases of Mechanochemical Technologies" (FBMT-2022) aims to present the latest research and results of scientists related to application of the mechanical activation methods for the fabrication and design of new materials and creation innovative mechanochemical technologies. This conference provides opportunities for the different areas delegates to exchange new ideas and application experiences face to face, to establish business or research relations and to find global partners for future collaboration.

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METASTABLE STRUCTURE AND PROPERTIES OF FUNCTIONAL NANOCOMPOSITES PREPARED VIA AN AFFORDABLE MECHANOCHEMICAL ROUTE

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This short review introduces three case studies for functional nanocomposites prepared via mechanochemical routes, i.e., i) molecular dispersion for pharmaceutics with retarded recrystallization kinetics, ii) nano-glassy and nano-crystalline complex oxides for electromagnetic applications, and iii) mechanosynthesis of double perovskite with high anti-site disorder. Mechanisms of apparent stabilization of intrinsically metastable products are discussed. Some remarks are given toward affordable material processing, irreplaceable by other nonconventional chemical processes.

APPLICATION OF MECHANICAL ACTIVATION IN SHS-TECHNOLOGIES OF HIGH-TEMPERATURE CERAMICS

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Elemental SHS and filtration combustion of mechanically activated (MA) mixture facilitates producing the single-phase and heterophase unique products. The comprehensive approach for modeling of SHS process and structural transformation was discussed. This approach involves ab initio grand potential modeling, Ellingham diagrams, phase predominance diagrams, and can correctly predict the peculiarities of phase and structure formation even in multicomponent mixtures with complex and convoluted reaction pathways. Using Zr-Ta-B, Zr-Ta-Si-B systems, as an examples, we predicted and experimentally verified the formation and decomposition of transient Ta_5Si_3 phase in the combustion front, emergence of Ta_3B_4 phase in the post combustion zone, and formation of peculiar microgradient grain structure with distribution of Ta and Zr within the grains of solid solution.

The resulting hot pressed boride ceramics were characterized in terms of their mechanical properties, thermal conductivity, oxidation resistance. The single-phase solid solution $(Hf,Ta)B_2$ demonstrates a superior combination of hardness 70 MPa, elastic modulus 584 GPa, thermal conductivity 53 W/m·K, and his composition with SiC has a high thermal oxidative resistance with decomposition enthalpy.

The carbide single-phase solid solutions (Ta,Zr)C, (Ta,Hf)C, (Ta,Zr,Hf,Nb,Ti)C showed a notable growth of properties. MA of reaction mixtures in the system Me^{IV}-B-C made it possible to synthesize eutectic $Me^{IV}B_2$-$Me^{IV}C$ ceramics with ultra-fine grain size structure. The depth of transformation does not linearly depend on the duration of MA. Depending on the MA modes, the proportion of the fraction smaller than 1 μm varied from 50 to 10%.

Effect of MA was observed also on structure, particle size distribution of SHS-powders and properties of hot pressed Ti(C,N)-Si_3N_4-SiC ceramics.

This work was carried out with financial support from the Russian Science Foundation (project no. 19-19-00117).

THE STUCTURAL DISORDER–MAGNETISM RELATIONSHIPS IN MECHANOSYNTHESIZED NANOOXIDES

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The interplay of magnetism and structural disorder in mechanochemically processed complex oxides is a fascinating subject of recent interest [1, 2]. The present work reviews a one-step mechanosynthesis and magnetic properties of magnetoceramics with a variety of structure types (cubic spinel, orthorhombic olivine, perovskite, hexagonal structure, double perovskite). The case studies are presented, focusing on recent progress in a fundamental understanding of the structural disorder–magnetism relationships in "interface-controlled" complex oxides prepared by mechanochemical routes. The far-from-equilibrium structural disorder in iron containing magnetic nanomaterials is studied by means of ^{57}Fe Mössbauer nuclear probe spectroscopy. The functional behavior of mechanosynthesized oxides is characterized by SQUID measurements. Selected examples of the separation of interfacial/surface effects from bulk effects in oxide nanoparticles are presented. It is demonstrated that interfacial effects in the mechanosynthesized ceramics may result either in an enhancement of magnetic behavior or in its degradation, *i.e.*, in a desired or undesired magnetic property modification, when compared to magnetism of their bulk counterparts prepared by a conventional ceramic method.

The present work is supported by the DFG (project SE 1407/4-2).

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SHOCKWAVE CHEMISTRY AND ITS APPLICATION IN CARBON NANOMATERIALS SYNTHESIS

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Shock loading takes materials from ambient conditions to extreme conditions of temperature and nonhydrostatic stress on picosecond timescales. In molecular materials, shock loading results in temporary nonequilibrium conditions with overheated low-frequency modes and relatively cold intramolecular modes with high-frequency, causing a series of catastrophic changes of material chemical and physical properties. These processes can conspire to lead to a material response not observed under quasi-static loads. Herein, systematic research on synthesis of various carbon-based nanomaterials has been carried out, considering the simple and effective technology of shockwave synthesis.

The controlled detonation of explosives mixed with different precursors or catalysts leads to efficient chemical reactions under extreme conditions and the synthesis of various nanocarbon materials. A Fe_3O_4-Fe@carbon nanotube composite was successfully synthesized through detonation of organic iron materials. Besides, the detonation of mixtures of organics, organic iron and explosives has been utilized to produce nanocarbon onions and carbon-encapsulated iron-based nanoparticles with a core-shell structure. Detonation-driven high velocity flyer impact loading was employed to induce shock wave for the synthesis of high-quality graphene materials. Using certain solid carbon sources, such as dry ice and calcium carbonate, graphene nanosheets were successfully synthesized by shock-induced reduction reaction through detonation-driven flyer impact. Furthermore, by adding ammonium nitrate to the reaction system, nitrogen-doped graphene materials were formed in this one-step shock-wave treatment.

Keywords: shockwave chemistry, synthesis, carbon nanomaterials, carbon nanotube, graphene

MECHANICAL ACTIVATION AND MECHANOCHEMICAL REACTIONS IN TECHNOLOGY OF METAL-ION BATTERIES

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High-energy solid-state mechanical activation (MA) is one of the modern and promising synthetic methods to prepare different nanostructured functional materials. This is due to the potential application of MA in technology, in particular, for the development of so-called dry processes, which are more environmentally friendly and cost-efficient than the currently adopted technologies and may be important for different applications including the production of electrode materials for metal-ion batteries (MIB). Technological benefits of mechanochemical synthesis are enhanced by a combination of MA (excitation) with subsequent thermal treatment (relaxation). Some mechanochemical approaches have been developed, including acid-base reactions (so-called ‘Soft mechanochemical synthesis’ [1]) (e.g., to prepare $LiMn_2O_4$), mechanochemically assisted ‘selective carbothermal reduction’ (e.g., $LiFePO_4$) and ‘associated reactions’ between covalent and ionic compounds (e.g., $Na_3V_2(PO_4)_2F$), etc. Since the calcination temperature remains significantly lower than when a conventional method is used, the average size of the primary particles is less than 100 nm.

Meanwhile, in certain cases, direct mechanochemical synthesis of electrode materials for MIB can be carried out. In [2], the synthesis of a new nanostructured cathode material for lithium-ion batteries (LIBs) with the composition ‘$Li_4Mn_2O_5$’ and the disordered rock-salt structure was realized. It shows a discharge capacity of 355 mAh/g, which is the highest among the reported Mn oxides due to multielectron redox reactions. In the last few years, a new class of cathode materials for LIBs has been proposed based on Li-excess oxides and oxyfluorides with disordered rock-salt structure (DRX), in which Li and transition metal ions equally occupy octahehdral sites. Some of them can be also obtained by direct mechanochemical synthesis. Despite the disordered structure and the absence of diffusion channels, they are characterized by a high specific capacity >200 mAh/g.

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EFFECTS OF FOREIGN SiCp PARTICLES ON UNDERCOOLING TRANSFORMATION AND HIGH TEMPERATURE PERFORMANCES IN CAST ALLOYS

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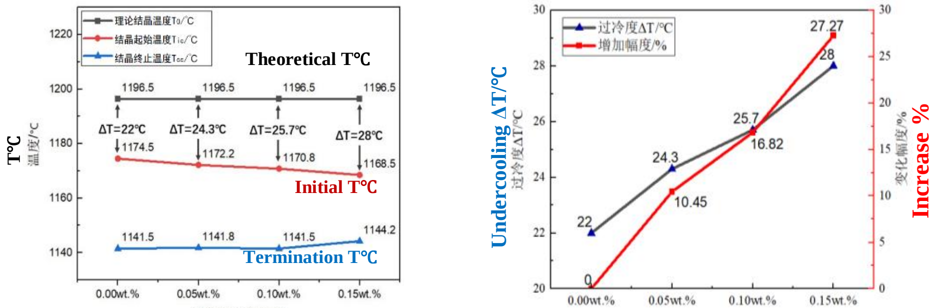
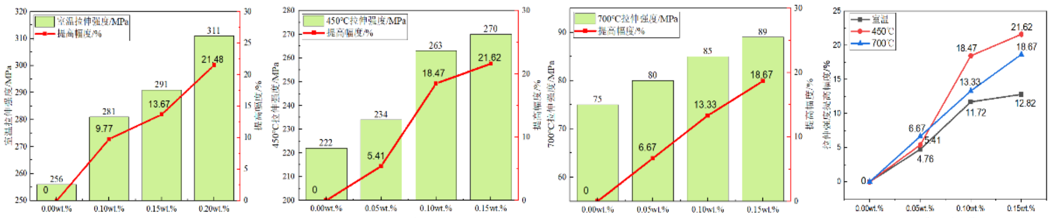
Although the researches on reinforcing casting alloys with foreign refractory particles has been carried out in Russia and China for more than 20 years. There are still some problems that are not clear enough, such as the reason for almost all mechanical and chemical properties can be improved at the same time; why it is applicable to all kinds of casting alloys; Especially, the high temperature properties and solidification process of castings are still lack of investigations. The present paper summarized our results during last few years, especially the undercooling transformation during solidification and high temperature properties, so as to promote both of the theoretical and application studies further.



(a) Effect of activated SiCp on crystallization temperatures

(b) Effect of activated SiCp on undercooling

Fig. 1. Effect of SiCp on Unercooling Transformation.



(a) At room temperature

(b) At 450°C

(c) At 700°C

(d) Increase rate at different T℃

Fig. 2. Effect of Activated SiCp on High Temperature Tensile Strength in Gray Cast Iron.

AN OVERVIW OF THERMALLY SPRAYED Fe-BASED METALLIC GLASS COATINGS: FROM THE ALLOY DEVELOPMENT TO THE COATING'S PERFORMANCE AGAINST CORROSION AND WEAR

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Fe-based bulk metallic glass (BMG) presents unique tribological and electrochemical properties. Given the inherent brittle nature and dimensional limitations of Fe-based BMGs, technological and scientific efforts are focused on their use for surface engineering solutions. Fe-based BMG coatings are promising to protect steel components operating in a wide array of hostile environments, with encouraging resistance against corrosion and wear. This article summarizes the progress of Fe-based glassy coatings in terms of alloy design, glass-forming ability, crystallization, powder production, thermally-sprayed coatings, and how the microstructural features dictate the basket of properties. The strategy for selecting the alloy composition with high glass-forming ability is discussed based on thermodynamic calculations. Two main methods are presented for feedstock powder production: gas-atomization and high-energy ball milling. Different processing routes to produce Fe-based coatings and deposits are summarized: detonation spraying, high-velocity oxygen fuel, flame spraying, non-vacuum electron beam cladding, and spray forming. The resulting phases (glassy and crystalline), microstructures, porosity levels, and hardness values are comparatively discussed and related to the corrosion and wear resistances. The final part of the work is dedicated to a new generation of Fe-based BMGs that emerged as contender to further enhance the corrosion and wear resistances.

A GREEN ALTERNATIVE FOR POTASH EXTRACTION FROM GLAUCONITE USING MECHANICAL ACTIVATION

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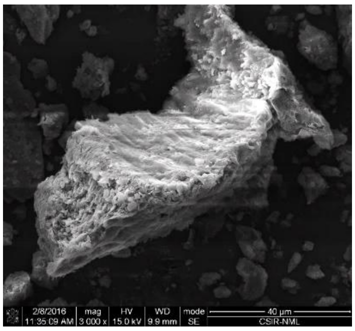
Glauconite [(K, Na, Ca) $(Fe^{3+}, Al, Mg, Fe^{2+})_2(Si, Al)_4O_{10}(OH)_2$] is a low-grade mineral resource for potassium (K_2O content ~ 4-7 %) (Fig. 1). The focus of this presentation is on the mechanical activation (MA) of glauconite using a planetary mill. The emphasis is on physicochemical changes and their effect on cation exchange capacity, notably potassium.



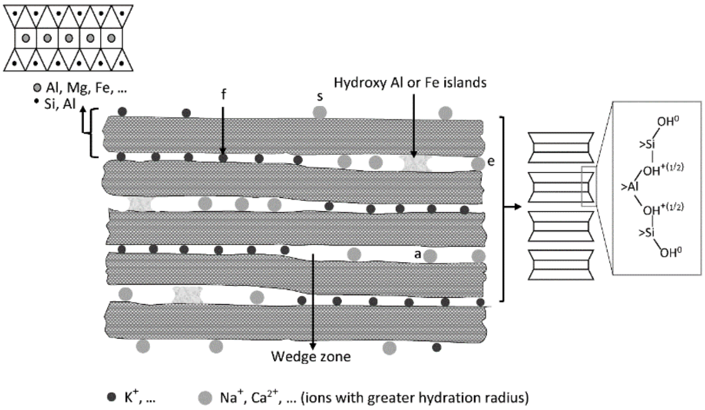


Fig. 1. Glauconite morphology and structure [1]

The cation exchange capacity (CEC) of glauconite (an important measure to assess the direct application of glauconite as fertilizer) improved remarkably with milling. Typically, after 2 h of milling, total CEC increased from 43 to 105 meq/100 g (~ 2.5-fold increase), attributed primarily to the increase in exchange capacity of K^+ ions from a negligible value to ~ 65 meq/100 g. The effect of milling time on the exchange behaviour was ion-specific; unlike K^+, the CEC of Na^+ and Ca^{2+} decreased and, Mg^{2+} showed an initial increase (up to ~ 60 min) and then decrease with prolonged milling. The CEC is correlated with the physicochemical properties of the samples milled for the different duration and, a plausible explanation for ion-specific response is presented. The presentation will highlight the superiority of the MA approach over chemical methods of potassium recovery.

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GEOPOLYMERS BASED ON MECHANICALLY ACTIVATED FLY ASH BLENDED WITH ALKALINE EARTH METAL CARBONATES

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Synthesis of geopolymer materials based on coal fly ash (FA) is a subject of active research in the last decade. Geopolymers, also referred to as inorganic polymers, are a subclass of alkali activated materials prepared by the reaction of natural and industrially produced aluminosilicates, with an alkaline agent (e.g., alkali metal hydroxide solution or liquid glass) at near ambient temperatures. Because of energy saving, environmentally benign processing, and high performance, geopolymers have received attention in construction engineering as a promising substitute to traditional Portland cement. Besides, geopolymers are considered as matrices for immobilizing heavy metals and radioactive waste, as fire-resistant and radiation-resistant materials.

The aim of this study is to investigate the influence of alkaline earth carbonates (MCO_3, M – Mg, Ca, Sr, Ba) addition to the FA and mechanical activation (MA) on the compressive strength of geopolymers based on these mixtures. Sodium hydroxide solution was used as an alkaline agent. MA was carried out in a planetary mill. MA of the raw material considerably enhanced its reactivity with respect to the alkaline agent, as was observed using FTIR spectroscopy, isothermal conduction calorimetry, thermogravimetry, and SEM/EDS. In terms of geopolymer compressive strength, the highest positive effect of carbonate additive to the FA was observed for calcite $CaCO_3$. It was shown that the addition of up to 10% calcite or dolomite to the FA and the subsequent MA of the mixture significantly increased the compressive strength of the geopolymers, and a synergistic effect of the two factors was observed. The addition of Mg, Sr, and Ba carbonates to FA was less effective. A simple method for evaluating the increments of MA, carbonate additives, and a synergistic effect in the increase in the compressive strength of the composite geopolymers has been proposed.

This study was funded by RFBR, project number 20-03-00486.

MECHANOCHEMICAL DESTRUCTION OF ORGANIC POLLUTANTS: HOW FAR HAVE WE GONE AND WHERE ARE WE GOING?

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Mechanochemical destruction of organic pollutants is growingly becoming a viable approach to safely dispose those organic pollutants (man-made or unintentionally generated mainly during some industrial processes) that pose a significant risk to human health and the environment, due to their high toxicity, remarkable persistence, and nonnegligible bioaccumulability in living tissues. High energy milling of such persistent organic pollutants (POPs) with a co-milling reagent for a relatively short time (few hours) allows the complete mineralization of POPs, which are transformed into amorphous carbon, carbon oxides, and halides. This mechanochemical treatment takes place at near room temperature, so, compared to thermal destruction technologies like incineration, it can avert unintentional formation of dioxins (if milling conditions are carefully selected). In addition, it can be used, in some cases, to produce valuable materials instead of detoxified waste. The complex reaction mechanism begins with formation of active species thanks to the mechanical activation of the co-milling reagent. Such active species attack the organic pollutant inducing its dehalogenation and generating organic radicals, which then give origin to a cascade of radical reactions that ends with the mineralization of the POP molecule. Finally, preliminary economic considerations suggest that the mechanochemical destruction is a feasible and economic technology to safely detoxify POPs.

MODELING OF IRREVERSIBLE PROCESSES IN ACTIVATED MATERIALS

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Modern methods of activation of initial mixtures in technologies of synthesis of new materials are essentially aimed at creation of nonequilibrium states of materials and their surfaces. The theoretical basis of modern methods of modifying the states of materials is nonequilibrium thermodynamics, within the framework of which it is possible not only to explain the change in the properties of materials under external influences, but also to predict the nature of their change. In [1], to describe irreversible processes under essentially non-equilibrium conditions, for example, the phenomena of mass transfer and related transformations of composition and structure, a new parameter - the activation parameter, characterizing the deviation of the system from the thermodynamic equilibrium state, was proposed and substantiated. Subsequent works were mainly aimed at studying the peculiarities of changes in the effective properties of activated materials under surface treatment conditions. However, the applicability of such an approach is not limited to electron-ion-plasma technologies.

The description of radiation-stimulated diffusion phenomena can be as an application of the theory [2]. Another example of the use of the theory can be an explanation of the phenomenon of relaxation of the properties of internal interfaces under isothermal annealing conditions. The effect of the nanoparticle fraction on the acceleration of reactions under thermal explosion conditions is explained in a similar way in [3].

Finally, using the activation theory, it is possible to explain some regularities of the synthesis of composites from a mechanically activated mixture of powders [4].

This paper analyzes possible approaches to describing the nonequilibrium kinetics of phase formation based on extensions of thermodynamics.

The work was supported by RFBR and ROSATOM, grant No 20-21-00064.

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NEW ERA OF MECHANO-SYNTHESIS: ALTERNATIVE STRATEGY ACCESS TO DRUG-ACTIVE MOLECULES

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Over the past century, innovations in synthetic chemistry plays a fundamental role in medicine chemistry that enabled the discovery and development of important life-changing medicines. However, environmental pollution and safety hazards during the development of chemical pharmacy raised much concern. The overuse of highly flammable and volatile organic solvents has caused significant damage to the environment. Though the low-toxic green solvents have been developed continuously, solvent-free or solvent-less reaction would be one of the most powerful ways to get over the problem.

Mechanochemistry, that induces chemical reactivity by mechanical force could promote the reaction between different phases without solvent or with only small drops of solvent [1]. This enabling technology was identified by IUPAC as one of 10 world-changing chemistry innovations and dubbed as chemical 2.0 [2]. Despite firmly established applications of modern mechanochemistry in new material preparation, cocrystallization and waste disposal, more attentions would be paid to mechanical procedures for generating pharmaceutically relevant fragments and functionalities. Herein, we would like to introduce our works of mechanosynthesis of drug-active molecules mainly related to cross-couplings, C-H functionalization, cross-dehydrogenative couplings (CDC) and addition reactions, which features step-economy, time-saving and green properties. We believed that with the development of equipment and detection techniques, mechanochemistry will blossom in pharmaceutical industry in near future.

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MECHANOCHEMICALLY PREPARED PHARMACEUTICAL SOLID DISPERSIONS FOR SUPRAMOLECULAR DRUG DELIVERY SYSTEMS. PHYSICO-CHEMICAL AND PHARMACOLOGICAL PROPERTIES

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Physicochemical and pharmacological properties of mechanochemically synthesized supramolecular systems/complexes of the "guest-host" type have been studied in the investigations of institutes of the SB RAS. The "guest" is a molecule of medicinal substances, and the "host" is a carrier particle - a macromolecule of polysaccharide, a glycoside micelle, particles of silicon dioxide, etc. The strengthening of the pharmacological effect of such structures is achieved by increasing the water-soluble and trans-membrane permeability of drug molecules. The most effective "hosts" of the studied carriers are plant metabolites – glycyrrhizic acid and its salts, as well as the polysaccharide arabinogalactan from wood of *Larix Siberica*. An original solid-phase mechanochemical technology has been developed to obtain supramolecular systems from solid dispersions of components. In this case, supramolecular systems are formed in the process of solid-phase synthesis, or by dissolving the obtained dispersions in aqueous media. As a result of studies of a large number of widely used drugs of various pharmacological classes, it has been shown that the inclusion of drug molecules in these supramolecular systems can significantly increase the bioavailability, effectiveness and safety of their action and significantly (by 2-150 times) reduce the effective therapeutic dose of drugs, reduce (up to complete disappearance in some cases) harmful side effects.

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MECHANOCHEMICAL TRANSFORMATIONS OF POLYSACCHARIDES: A SYSTEMATIC REVIEW

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Polysaccharides are a wide class of natural polymers having a long successful history of application for material science and a great potential for further use in a wide range of areas. Modification of polysaccharides’ chemical structure is expanding the number of technologies for their processing and, thus, the range of polysaccharide-based functional materials. Currently, the use of polysaccharides safe for humans and the environment attracts close attention as a key element of "green chemistry" in various fields as versatile constructional and biologically active functional materials. Polysaccharides also find their place in such modern areas of life science as additive technologies for the fabrication of three-dimensional scaffolds for regenerative medicine, and the creation of new drug delivery systems and biosensors.

In the last decade, there has been a significant increase in interest in the processes occurring in polymers under mechanical action. Taking into consideration the items of the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA), we reviewed application of mechanochemical approaches to the modification of polysaccharides. The search strategy incorporated examination of electronic database Scopus, eLibrary and in some cases the websites of journals and libraries to find the full-text of earlier documents. The works were focused mainly on: (1) mechanical activation of natural polysaccharide-containing sources; (2) mechanochemically assisted immobilization of non-/poorly-soluble bioactive compounds onto water-soluble polysaccharides; (3) mechanosynthesis of polysaccharide derivatives and copolymers and fabrication based on materials.

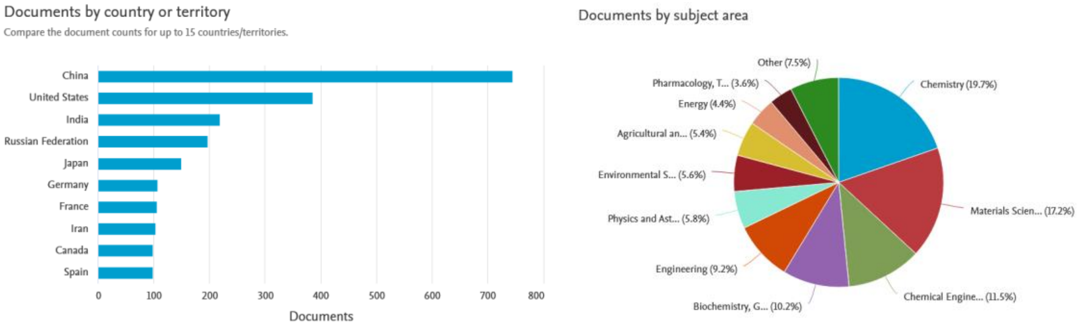

Fig. 1. Documents found in the Scopus electronic database using "Mechanochemistry or Mechanochemical" and "Polysaccharide" as keywords.

OXIDATION AND COMBUSTION OF COMPOSITE "WOOD-COAL" PARTICLES

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A review of the work of ISSCM and the Kutateladze Institute of Thermophysics SB RAS is presented. Composite particles with sizes less than 100 microns are characterized by a disordered fibrous structure of wood with distributed coal microparticles. The specific surface of the composite particles is 2.9 m^2/g, the degree of cellulose crystallinity is up to 40%.

Samples are oxidized in two main stages. At the first stage, the release and combustion of gaseous products occurs, at the second stage, the product of the first stage, carbon, is oxidized. An increase in the carbon content in the composite leads to a shift in the decomposition rate maxima.

The combustion of particles in air flows has been studied. The ignition delay time of the composite fuel has a non-linear dependence on the ratio between the components. The value of the ignition delay time for the composite is less than for other samples (coal, sawdust, mixture). The minimum flash point corresponds to 70% coal and 30% sawdust.

The composite burns better than the mixture - combustion begins earlier, the completeness of fuel combustion increases. When burning composite fuel, the first stage begins earlier than when using mixed fuel and occurs at temperatures 50–100 °C higher. Combustion in the second stage occurs approximately simultaneously for both the mixture of components and the composite fuel, but the combustion of the composite provides temperatures 100–400 °C higher. The formation of paramagnetic centers on the surface of particles during the preparation of composite fuel, is shown. The EPR signal from treated wood samples corresponds to the EPR signal from lignin.

A model of combustion of composite particles from coal and vegetable raw materials is presented, which includes two main stages. At the first stage, combustible gases are released from the thermally less stable internal component of the composite particle - vegetable raw materials. Combustion of combustible gaseous products of thermal decomposition is initiated by radical centers on the surface of coal particles. At the second stage, the combustion of carbon occurs, which is formed during the decomposition of plant materials and coal.

This work was supported by state assignment to the Institute of Solid State Chemistry and Mechanochemistry SB RAS (project No. 121032500067-9).

STUDY ON ANTIBACTERIAL PROPERTIES AND PREPARATION OF HIGH ENERGY ACTIVATED DIOSCOREA NIPPONICA MAKINO STARCH FILM

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An antibacterial starch film was prepared, which is based on the subsidiary resource Dioscorea Nipponica Makino starch, and added natural antibacterial ingredients such as chitosan, tea polyphenols, etc., and then mixed with fillers, plasticizers, etc., after swelling, plasticizing and pressing to obtain. The preparation process is to introduce high-energy activation process before the mixture swelling of each component, in order to improve the activation energy of the system, enhance the interaction between components, so that the properties of the film can be improved. We tested Dioscorea Nipponica Makino starch film using some methods, such as: polarizing microscope observation, contact Angle test, infrared spectrum analysis, tensile property test, SEM, TG-DSC, water vapor permeability test, soil degradation test, antibacterial performance test, and fruit preservation performance test, etc. By comparing the test results of samples with different formulas and high-energy activation or not processes, we found that adding chitosan and tea polyphenols affects the starch matrix continuity, which resulted in the reduction film tensile strength and water vapor transmittance increased, but the film has a certain antimicrobial property. On the other hand, we introduced high-energy activation in the preparation process, which improved the tensile strength, thermal stability of the film, and also improved the antibacterial and fresh-keeping effect of the film through the bacteriostatic and preservation tests, and at the same time reduced the water vapor permeability and soil degradation weight loss rate. By infrared spectrum analysis of dioscorea starch film, it was concluded that there was no new functional group, but the peak value of some functional groups shifted and enhanced, which indicated that high-energy activation increased the interaction effect of each component. Through the analysis of the antibacterial mechanism of dioscorea starch film, we concluded that high-energy activation increased the activation energy of the system, enhanced the activity of antibacterial components, and enriched the surface of some specific groups (such as -NH_2) and small molecules, which was conducive to inhibiting bacterial biological growth and improving the antibacterial property of the film. The high energy activated dioscorea starch has good film-forming property, higher air permeability of the film than pure starch film and lower than unactivated film, which ensures the gas supply for dormant respiration of fruit. It exactly verified by the test results of banana preservation.

Keywords: Dioscorea Nipponica Makino starch film; chitosan and tea polyphenols; high-energy activation; antibacterial and fresh-keeping effect

HIGHLY ANISOTROPIC MECHANICAL PROPERTIES OF MOLECULAR CRYSTALS – CURRENT MODELS, TECHNIQUES AND PROSPECTS

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Molecular crystals exhibiting the property of significant plastic deformation under mechanical action do not exceed 0.01% of the known crystal structures. Nevertheless, this property may turn out to be critical in mechanochemical processes, especially in the field of pharmaceuticals, and nanomaterials production. Understanding the principles of construction of structures with anisotropic mechanical properties, including bending crystals, opens up new horizons for the engineering of molecular crystals with desired properties.

An active systematic study of plastically "bending" crystals began in 2005 [1, 2]. Currently, experimental and computational methods are being actively developed. Experimental work is carried out using single-crystal diffraction, vibrational spectroscopy, nanoindentation, thermal analysis, microscopy, etc. Using these methods, a change in the spatial structure of deformed regions of crystals, intermolecular interactions and crystal morphology was established. Calculation methods in this area are focused on the study of individual intermolecular characteristics, as well as elastic moduli [3, 4].

Despite the active study of the phenomenon of significant plastic deformation, the current models explaining this effect are of a qualitative nature and do not involve quantitative estimates [5]. This work provides an overview of the area, discusses models in detail, and shows a trend in the study of bending crystals, primarily by computational methods, using several examples.

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MECHANOCHEMICALLY MODIFIED POLYSACCHARIDES AS STABILIZERS FOR EMULSIONS

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Emulsions are widely used for pharmaceutical applications and for fabrication of materials for regenerative medicine. For both these applications the naturally-derived biodegradable polysaccharides is highly desirable as an alternative to synthetic surfactants. Non-adsorbing polysaccharides are mainly used as thickening agents, tablet binders, etc., while only a few polysaccharides can adsorb at the oil/water interface to enhance stability of emulsions tailored for advanced applications. Modification of chemical structure of polysaccharides allows controlling their ability to stabilize oil/water emulsions and to wide areas of potential use.

This work is aimed at studying the ability of mechanochemically modified polysaccharides to stabilize the oil/water interface in a course of fabrication of polylactide microparticles via oil/water emulsion solvent evaporation technique. The preliminary screening of a range of polysaccharides (guar, arabinogalactan, hydroxyethyl cellulose, hyaluronic acid, chitosan, etc.) showed that the highest total yield was found for chitosan. Solid-state synthesis of chitosan’s derivatives and graft-copolymers was realized using twin-screw extruder. Substitution of chitosan amino groups by 2,2-bis(hydroxymethyl)propionic acid allowed to obtain a range of chitosan derivatives having a degree of substitution from 0.16 to 0.43. The total yield of the microparticles stabilized with chitosan derivative with the highest substitution degree increased in 2-times in comparison with microparticles stabilized with non-modified chitosan. Alkyl derivatives of chitosan were also synthesized in solid-state and successfully used as emulsifiers for microparticle stabilization. Grafting of oligo/polylactide fragments onto chitosan backbone provided the increased copolymer hydrophobicity. Chitosan-g-oligo/polylactide copolymers allowed to form a wide range of microparticles via emulsion solvent evaporation technique without additional emulsifiers in aqueous phase. The chitosan-g-oligo/polylactide-based microparticles were successfully used as cell microcarriers and building blocks for fabrication of 3D scaffolds.

MECHANICALLY ACTIVATED SHS AND MECHANICAL SYNTHESIS OF HIGH ENTROPY ALLOYS: AN OVERVIEW

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It is known that mechanical activation significantly affects reactive properties of powder mixtures, e.g., for self-propagating high temperature synthesis (SHS) [1-3]. Some recent data related to this matter are outlined and discussed briefly in this overview. First, mechanics of the milling bodies movement in the planetary mills have been studied by means of high-speed video. The data obtained leads to conclusion that dry friction and shear deformation are the main factors that influences an interdiffusion of metals, resulting to decreasing a reaction onset temperature and increasing of solid-state mechanical alloying rate. This concept is discussed by the examples of SHS powder mixtures [4] and high entropy alloys (HEAs) [5]. We consider mechanism of the mechanical synthesis of medium- and high-entropy alloys of 3d transition metals that has been studied both experimentally and theoretically in terms of molecular dynamic simulation. The synthesis was found to occur in two stages. The first stage involves a refinement of crystallites and accumulation of structural defects due to severe plastic deformation and friction of metal particles that induce abnormally fast diffusive mixing of different metal atoms. This process results in formation of nanocrystalline intermediate alloy with a crystallite size of about 10 nm. The second stage involves recrystallization that leads to the nucleation and growth of multicomponent phase(s) with a simple FCC or BCC structure. A critical time for the onset of recrystallization depends on planetary milling conditions. The mechanically alloyed HEAs can be used as components for SHS of some ceramic-metal composites. These results open up a route to time-consuming and facile mechanical synthesis of high-entropy materials.

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FEATURES OF STRUCTURAL-PHASE TRANSFORMATION OF METAL POWDER MIXTURES UNDER HIGH-ENERGY MECHANICAL ACTIVATION

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Structural-phase transformations occurring under conditions of energy-intensive mechanical activation are demonstrated on the example of binary (Ni-Al, Nb-Al) and multicomponent (W-Ta-Mo-Nb-V-Zr-Cr-Ti, W-Ta-Mo-Nb-Zr-Cr-Ti) mixtures of metal powders.

In addition to grinding and mixing of the initial components of powder mixtures, the formation of highly defective, including submicrocrystalline and nanocrystalline structural states, is observed, similarly to metallic materials under conditions of severe plastic deformations (torsion under pressure, deep rolling, etc.). As is known, such states are characterized by a high density of defects in the crystal structure, and the presence of nonzero values of the components of the bending-torsion tensor indicates the implementation of cooperative dislocation-disclination mechanisms of crystal lattice transformation.

In binary systems of the Ni-Al type, the formation of a Ni(Al) solid solution was found already at the early stages of processing, followed by a “low-temperature” synthesis of the Ni_3Al intermetallic phase. An increase in the duration of mechanical activation is accompanied by an increase in the volume fraction of Ni_3Al and the appearance of other high-temperature intermetallic phases.

In the studied multicomponent systems based on refractory metals, regardless of the degree of equiatomicity, an increase in the duration of mechanical activation contributes to the gradual transition of the precursor to a single-phase state in the form of the main BCC phase.

The formation of highly defective structural states is one of the main factors contributing to the synthesis of intermetallic compounds and the formation of solid solutions under conditions of low diffusion mobility.

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SYNCHROTRON RADIATION INVESTIGATION OF THE RAYLEIGH-TAYLOR EFFECT INITIATED BY MECHANOCHEMICAL IMPACT ON A SOLID

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The study of shock wave processes occurring during mechanochemical interactions is extremely important for understanding the mechanism of reactions and developing new technologies. In particular, it is necessary to understand the possibility of realizing the Rayleigh-Taylor instability in mechanochemical processes. During the development of this instability, a spontaneous increase of pressure and density perturbations occurs at the interface between two media with different densities, which are in the field of force action. A special case of instability is the instability at the boundaries of media with different densities when a strong shock wave reaches the free surface of the sample. Such an impact leads to the emission of a cloud of particles. This phenomenon is called "dusting".

Experimental study of these processes by traditional methods is difficult due to low densities (0.1–100 mg/cm^3), small sizes (1–30 μm), and high velocities of their flight (2–5 km/s). Therefore, since the 2000s, “dusting” has been studied using synchrotron radiation (SR). A feature of this work is the simultaneous use of two techniques - laser PDV and synchrotron radiation radiography. Synchrotron X-ray pulses have the same parameters (duration 1 ns, repetition period 124 ns) for a long time, which makes it possible to measure masses (and densities) with record accuracy when a cloud of microparticles moves after impact. Based on the data obtained, it can be concluded that when using the SR technique, it is possible to register a low-density cavity between the free surface and the main mass of the cloud of microparticles. From the measured speed of the tantalum foil (by the PDV method), the mass of dust that hits (arrives) on this foil was calculated. Using the small-angle X-ray scattering method, it was found that for some materials the dust cloud consists of nanoparticles.

MECHANICAL ACTIVATION IN PRODUCTION OF Ti MATRIX COMPOSITES REINFORCED WITH SUBMICRONE CARBIDE PARTICLES

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Mechanical activation (MA) of powder reagents promotes chemical reactions in the mixes strongly. A lot of the intermetallics and refractory compounds (carbides, borides, silicides) have been synthesized by using of preliminary MA of «metal - metal» or «metal - nonmetal» powder mixes. It seems to be prospective to apply MA for the production of metal matrix composites (MMC) reinforced with fine hard particles of the refractory compounds. Titanium carbide is of particular interest as a strengthening phase in the MMC and especially in titanium matrix composites. It is known, that the most advantageous combination of hardness, strength and ductility show the composites strengthened with 10 vol. % TiC particles of nano- or submicron size and spatially homogeneously distributed over the titanium matrix. According to assessments 10 vol.% $TiC_{0.5}$ in the Ti matrix composite corresponds to 1.0 mass.% carbon in Ti-C powder mixture. However the real carbide content turned out to be 10 times more in the Ti-C powder mixture subjected to MA in the planetary ball mill (60 minutes treatment at 755 rpm.) followed heating to 900 ^{0}C in 0.01 Pa vacuum. Moreover, 10 vol.% $TiC_{0.5}$ was detected by means of XRD analysis after heating to 900 ^{0}C of the mechanoactivated in the ethanol media Ti powder without carbon doping. The ethanol was added into the vials to avoid Ti powder sticking to the balls and to the vials walls. Titanium carbide emergence in the mechanoactivated titanium powder without carbon additive leads us to the assumption about ethanol destruction under intensive MA. This assumption is confirmed by the fact that titanium carbide was not detected in the MA Ti powder treated in ethanol free media.

Mechanoactivated in the ethanol media titanium powders were encapsulated into vacuum tight steel container and subjected to compression after heating for 15 min. in the furnace at 900 ^{0}C. As a result compacted sheets of Ti+10 vol.% $TiC_{0.5}$ composite with 0.5 % residual porosity were obtained. Hardness and bending strength of the composite sheets were higher and ductility lower than that of the sheets compacted from Ti powder not subjected to the treatment in the mill. The reason is strengthening and simultaneously embrittlement of the compacted titanium with carbide particles synthesized while heating of Ti powder mechanoactivated in the ethanol media.

GRINDING AND ACCUMULATION OF ENERGY OF MECHANICAL IMPACT IN THE DISINTEGRATOR

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The use of modern grinding devices with a high intensity of mechanical processing makes it possible to increase the reactivity not only by increasing the specific surface, but by activating them as a result of the occurrence of numerous defects in the crystal lattice. As a result, the energy barriers for the passage of chemical reactions are significantly reduced, and the energies of melting and decomposition of substances are reduced. In this work, it was found that mechanical processing of materials with different types of chemical bonds (NaCl, KCl, Si, Fe_2O_3, BaO_2, CaO_2, $Y_1Ba_2Cu_3Ox$, glass) in a disintegrator leads to significant grinding to micron sizes. Along with grinding, the process of energy accumulation by dispersed particles of different chemical nature in the disintegrator is observed, a different nature of energy accumulation is found, accompanied by the appearance of microdeformations and a change in block sizes. It has been established that as a result of shock effects in the disintegrator, distinct exothermic peaks are observed on the curves of differential thermal analysis and differential scanning calorimetry, indicating the process of energy accumulation as a result of the formation of defects in the crystal lattice structure.

The results of experimental studies of the processes of energy accumulation in substances with different types of chemical bonds through impact action indicate the different nature of its accumulation in covalent, ionic-covalent and the absence of energy accumulation in the simplest ionic crystals. The observed results of thermal and structural studies of substances indicate the different nature of structural disturbances that have arisen during mechanical processing in free impact modes. Experimental data on the retention of excess enthalpy values for a long time can be used to determine the time during which substances processed in mills remain active.

MECHANOCHEMICAL RECRYSTALLIZATION: FORGOTTEN BASICS AND NEW POSSIBILITIES

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The report relates to the field of mechanochemical synthesis, in particular, to the preparation of sulfur-containing nanocomposites of silver halides (AgX, X = Cl, Br, I) [1].

The aim of the study is to update the approach, rethink, develop and introduce into scientific practice the method of "mechanochemical recrystallization" in solid-phase systems with small additives of the liquid phase of the solvent, solid-phase precursors of reagents, and diluent [2] to stabilize the resulting nanoparticles.

The presentation is provided on the example of mechanical activation of the $AgNO_3-NH_4I-S$ system with dimethyl sulfoxide (DMSO) additives, and the result is the mechanochemical synthesis of sulfur-containing AgI / S nanocomposites with a controlled content of nanosulfur. The predetermined content of nanosulfur in nanocomposites is ensured by the process of dissolution-crystallization (recrystallization) of any types of sulfur in DMSO in a mechanochemical reactor [3].

AgI / S nanocomposites were obtained by a single mechanical treatment in planetary ball mill Pulverisette 5 with stainless steel fittings and from powders of precursors – $AgNO_3$ (≈1.7 g), NH_4I (≈1.5 g), NH_4NO_3 (diluent, ≈4.5 g), commercial sulfur (≈2.3 g) and DMSO (1÷3 mL). Samples of AgI / S (after 3-fold washing of the water-soluble of mechanosynthesis components with water using a centrifuge and drying of the resulting target product for 24 hours at 70°C) were studied by XRD ($D \sim 20$ nm; $\varepsilon \sim 0.2\%$), Raman Spectroscopy (confirmation of the qualitative composition), SEM-TEM-EDAX (morphology, dimensions, texture and numerical elemental composition of nanocomposites).

The results and references to similar approaches to this method are also given.

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SYNTHESIS AND PROPERTIES OF HIGH-ENTROPY CERAMICS

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High-entropy materials are one of the most popular areas of advanced materials science, substitution conventional approaches to creating new alloys that have practically exhausted their capabilities. High-entropy materials are defined as alloys or compounds consisting of five or more basic elements in the same molar ratios. Recently, the range of high-entropy materials has been expanded to include non-metallic and non-oxide elements and a class of high-entropy carbides, borides, nitrides and carbonitrides has been created.

In this work, carbides and nitrides of equimolar compositions, for example (TaTiNbZrHf)C and (TaTiNbZrHf)N obtained by a combination of high-energy ball milling (HEBM), self-propagating high-temperature synthesis (SHS) and spark plasma sintering (SPS). The influence of HEBM modes on the morphology, structure and phase composition of powder mixtures has been studied. Optimization of the planetary ball mill process allowed to obtain two types of powder mixtures: 1) reaction powders Ta/Ti/Nb/Zr/Hf and (Ta/Ti/Nb/Zr/Hf)/C for subsequent SHS; 2) products of mechanochemical synthesis - (TaTiNbZrHf)C. SHS features of the structure formation process in 4- and 5-component reaction mixtures were identified and studied. The obtained bulk ceramics were comprehensively characterized, mechanical properties, oxidative resistance in air and melting point (TaTiNbZrHf)C were investigated.

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POST-TREATMENT OF COLD SPRAY DEPOSITS BY FRICTION STIR PROCESSING

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Cold spray is the solid-state material deposition technology. In this process, the metal particles accelerated in supersonic gas flow impact the surface at the velocity 600-1200 m/s. The powders adhere to the surface due to local material recrystallization of the particle induced by high-speed plastic deformation during impact. [1]. The properties of cold spray deposits significantly differ from the reference values measured for the bulk material. In particular, due to specific structure of the particle-particle interface and small grain size at the particle periphery, the ductility of cold spray deposits is very low [2]. Application of friction stir processing (FSP) could be applied for post-processing of cold spray deposits in order to improve their mechanical properties. In FSP process, a rotating tool inserted into the material generates the frictional heating contact. During tool movement along the contact line, plastic material flow occurs at a temperature below the melting point as for cold spray. The plastic flow transfers the material from the advancing side to retreating side, leading to the formation of a stirred region [3].

In this study the FSP process is used for post-treatment of cold spray deposits produced from copper, stainless steel and mixtures of different powders. It was shown that important mechanical load during FSP process significantly modifies the microstructure of obtained coatings. In particular, in case of copper and stainless steel deposits the interfaces between particles disappeared and new fine grain structure was created. In case of FSP treatment of multicomponent coatings the intensive material mixing with formation of new phases was detected. The perspective of application of FSP process for synthesis of high-entropy alloy phases in cold spray composite coatings is discussed.

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MECHANISMS OF PHASE AND STRUCTURE FORMATION DURING SHS OF MAB PHASES BASED CERAMICS WITH PRELIMINARY MECHANICAL ACTIVATION

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Binary transition metal borides are known for their high melting point, hardness, electrical and thermal conductivity, inertness in many aggressive media, and sometimes magnetic properties. In combination with the third element, borides and carbides can retain or form atomic layered structures. Like the more well-known MAX phases (M denotes an early transition metal, A is a mostly IIIA or IVA group element, and X is either C or N), the nanolaminated MAB phases consist of a transition metal boride sublattice interleaved by a monolayer or bilayer of pure Al atoms. MAB phases are a family of triple layered compounds with an orthorhombic crystal lattice, where M is a transition metal; A - aluminum or zinc; B - boron.

At the moment, there are publications on the successful MAB phases preparation with the chemical formulas MAlB, M_2AlB_2, $M_3Al_2B_2$, M_3AlB_4 and M_4AlB_6, where M is Mo, W, Cr, Mn, Fe, Ru, Cr. Ternary borides with the compositions MoAlB, Fe_2AlB_2, and Mn_2AlB_2 were obtained by the self-propagating high-temperature synthesis (SHS) method in the thermal explosion mode.

In this work, studies were carried out on the preparation of a new class of boride ceramics based on MAB phases by the SHS method in the layer-by-layer combustion mode using preliminary mechanical activation (MA). The macrokinetic features studies of the reaction mixtures combustion depending on the initial temperature have been carried out. The MA effect on the mixtures reactivity, their structural and chemical homogeneity, on the combustion parameters and structural-phase transformations in the combustion wave was studied. The combustion front quenching method and dynamic X-ray diffraction analysis were used to study the staging of structural-phase transformations in the SHS wave. Compact ceramic samples have been obtained and their structure, mechanical properties, and oxidation kinetics have been studied.

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SHOCK SYNTHESIS OF BIMETAL OXIDES

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Shockwave actions induce multiple extreme phenonmena such as high pressure and high temperature, leading to changes of interatomic distances and electronic shell configurations and formation of novel materials. Bimetal oxides are important functional semiconductor materials, featuring low cost and outstanding properties owing to the coupling effect of two metal elements.

In this study, several bimetal oxides materials with formula of $A_2B_2O_7$ have been obtained through ball-milling treatment and shock loading. The precursors were ball-milled for mixture and activation, and then were treated by a shock-driven flyer. Through this approach, $Gd_2Zr_2O_7$, $La_2Ti_2O_7$ and $In_2V_2O_7$ are synthesized successfully. The influence of experimental conditions, such as duration of ball-milling, shock pressure and shock temperature, on formation of bimetal oxides are investigated. The actions of corresponding conditions are discussed based on experimental and characterization results. Our investigation demonstrates the high potential application of shock-induced reaction on synthesis of novel materials, including the preparation of new bimetal oxides.

Keywords: shock synthesis, bimetal oxide, shock-induced chemical reaction

A HIGH-PERFORMANCE AND LOW COST NITROGEN – CONTAINING GRAY CAST IRON

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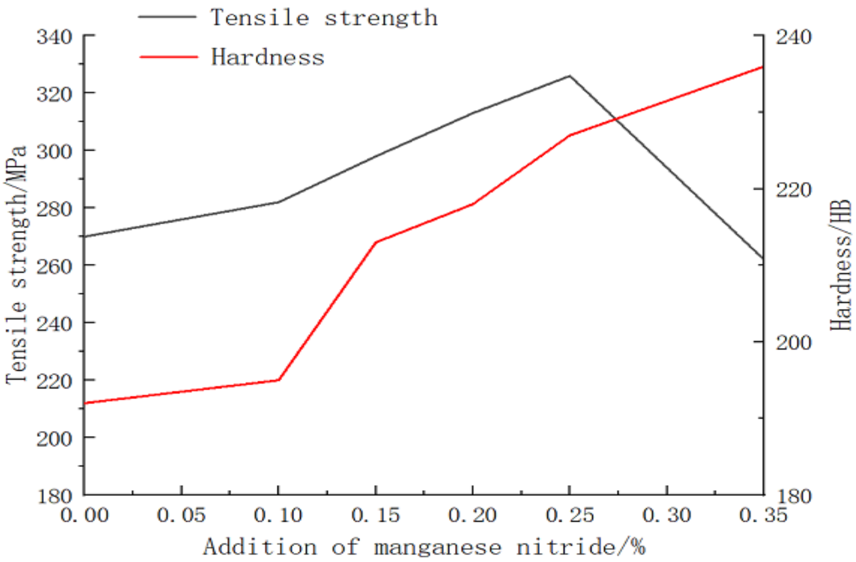
To meet the demand for high-strength gray cast iron castings while lowering casting production costs, nitrogen micro alloyed gray cast iron with manganese nitride inoculant was developed, and the effects of manganese nitride addition on its microstructure, mechanical properties, and casting cost were investigated. The test results show that with other manganese nitride additions, the graphite flakes have rounded ends and short, thick, and slightly curved shapes; as the nitrogen content in the iron increases, the graphite forms become more temporary and curved, and the pearlite content increases, which is conducive to improving the strength and hardness of gray cast iron. Excess nitrogen content in castings causes nitrogen porosity defects, significantly degrading material properties. The addition of alloying elements such as Cu and Sn can be reduced by adding an appropriate amount of manganese nitride to the process. The casting cost can be reduced by 180 RMB/ton to realize low-cost production of high-performance gray cast iron.

Keywords: Gray cast iron; nitrogen element; microstructure; mechanical properties; cost of production



Mechanical Properties of Gray Cast Iron under Different Manganese Nitride Content

FORMATION OF HIGH-ENTROPY TiVNbMoTa, TiVNbTaW ALLOYS DURING MECHANICAL ALLOYING

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Refractory high-entropy alloys (HEAs) are promising high-temperature structural materials for the aerospace industry due to their high melting point and strength. Mechanical alloying (MA) makes it possible to synthesize multicomponent alloys with a uniform distribution of elements, which is an advantage of this method compared to arc melting [1–3].

In this work, high-entropy alloys based on refractory metals (Ti, V, Nb, Ta, Mo, W) were obtained by mechanical alloying of the powder mixtures in a planetary ball mill after relatively short time (30 – 180 min). The MA was carried out in Ar atmosphere, with balls-to-powders mass ratio 20:1 and rotation speed 900 rpm.

X-ray phase analysis showed that in the Ti-V-Nb-Mo-Ta system, the formation of a single-phase solid solution with a bcc structure occurs after 30 minutes of activation. In the Ti-V-Nb-Ta-W system, the formation of a solid solution with a bcc structure occurs after 60 minutes of activation. Studies of powder sections by SEM showed that at these activation times individual fragments of the original metals still remain in the alloy particles, and a single-phase alloy with a uniform distribution of all elements in the Ti-V-Nb-Mo-Ta, Ti-V-Nb-Ta- W is formed only after 180 minutes of mechanical activation.

To obtain bulk HEAs, alloy powders were consolidated by spark plasma sintering (SPS) in vacuum at 1300 °C or conventional sintering in an argon atmosphere. Almost pore-free materials obtained during sintering retained the bcc structure of solid solutions.

The average microhardness values of the TiVNbMoTa and TiVNbTaW alloys sintered after 180 minutes of MA were 6 and 8.5 GPa, respectively.

The study was financially supported by the Russian Science Foundation (project no. 20-13-00277).

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OBTAINING OF NON-EQUILIBRIUM HARD ALLOYS BY EXPLOSIVE PRESSING OF POWDERS

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The paper presents the results of the experimental investigations the possibility of obtaining the consolidated powders of hard alloys by explosive pressing without subsequent sintering. It is found that the main factor determining the compaction of powder mixtures containing refractory carbide particles and metal ligaments in their composition is the dynamic flow of the ligament into the gaps between the carbide particles. In this case, the degree of compaction of powder mixtures is determined by the possibility of shock waves in the metal bond particles to their free from contact with other particles of the surface and the mass velocity acquired by the bond on these surfaces due to unloading.

It is shown that in contrast to the calculated equilibrium composition of the explosive compression in solid alloys of chromium carbide and titanium, obtained by heating the powder mixture in shock waves from 300˚C to 600˚C, the phase composition is fully consistent with the composition of the original powder mixture – Cr_3C_2 and Ti. When heating the powder mixture in shock waves in excess of 600˚C, on the limits of the carbide particle phase composition is changed: it starts a chemical reaction of the starting components with the formation of titanium carbide $TiC_{0,59}$ and chromium carbides Cr_7C_3, $Cr_{23}C_6$. The thickness of the boundary layers does not allow to study in detail their composition and structure by standard methods of scanning electron microscopy.

An increase in the heating of the powder mixture in shock waves to a value of about 1000 ˚C leads to an intensive macrochemical interaction of the powder mixture components and the formation of a phase composition corresponding to the equilibrium calculated by thermodynamic modeling methods. The reason for the intensive interaction is related to the unsteadiness of the shock wave front shape at the time of its formation in the powder mixture, which leads to the localization of particle deformation and the appearance of jet flows that cause local overheating of individual micro-volumes of the pressed material up to its melting. The appearance of the liquid phase is accompanied by the dissolution of the particles of the initial chromium carbide Cr_3C_2 and the formation of a new equilibrium structure at high pressure, which persists during subsequent cooling.

RECENT PROGRESS IN METAL MATRIX COMPOSITES OBTAINED BY SPARK PLASMA SINTERING OF POWDER BLENDS AND HIGH-ENERGY BALL-MILLED MIXTURES

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The topic of this talk is the development of metal matrix composites (MMCs) by spark plasma sintering (SPS) of powder blends and high-energy ball-milled mixtures [1, 2]. A brief overview of recent achievements of the international community is followed by the presentation of research activities conducted at ISSCM SB RAS and LIH SBRAS in the past few years in this area. Both reactive sintering processes and those not involving chemical reactions are considered. The morphology of the particles is a crucial factor in the development of the sintered microstructures. The morphology of the particles can be tailored by varying the duration of high-energy ball milling [3]. The effects of overheating at the inter-particle contacts during SPS are examined using reactive and non-reactive systems. The influence of pressure applied during SPS on the microstructure of the sintered MMCs is discussed.

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EFFECT OF PRELIMINARY MECHANICAL MILLING ON THE MICROSTRUCTURE AND PROPERTIES OF Al-$Fe_{66}Cr_{10}Nb_5B_{19}$ COMPOSITES OBTAINED BY SPARK PLASMA SINTERING

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The target properties of Al and Al alloy matrix composites are specific strength, wear resistance and corrosion resistance superior to those of the unreinforced matrix. Recently, metallic glasses have been used successfully as reinforcing phases in Al and Al alloy matrix composites. The glassy metals are known for their high strength and high resistance to wear and corrosion. One of the key problems of the development of metal matrix composites is to distribute the second phase particles in the matrix. When added in low concentrations, coarse reinforcing particles are not efficient for mechanical strengthening. The finer the reinforcing particles are, the more difficult it is to evenly distribute them in the matrix. Mechanical milling (MM) is one of the possible solutions to the abovementioned problem. During MM, the particles of the starting powders not only mix with each other but can also decrease in size. It is of interest to investigate the microstructural changes occurring during MM of metal – metallic glass powder mixtures. It was shown that MM can lead to a significant improvement of the strength of the sintered material relative to the unreinforced matrix. In the present work, the influence of the preliminary MM on the microstructure and properties of spark plasma sintered Al-$Fe_{66}Cr_{10}Nb_5B_{19}$ powder mixtures has been demonstrated. Spark plasma sintering of the milled powders resulted in the formation of composites, in which the $Al_{13}Fe_4$ intermetallic phase formed owing to a reaction of Al with the Fe-based alloy. The composite sintered from the milled Al-20vol.%$Fe_{66}Cr_{10}Nb_5B_{19}$ mixture shows a hardness of 250±20 HV, a compressive yield strength of 735±5 MPa and a deformation at the maximal stress of 2%, demonstrating a significant improvement in strength relative to the reinforcement-free aluminum.

Mg, Mg-ALLOYS, AND Mg COMPOSITES PRODUCTION BY HIGH ENERGY BALL MILLING AND SEVERE PLASTIC DEFORMATION AIMING HYDROGEN STORAGE: CHALLENGES AND STRATEGIES

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In the last 20 years, Mg-based hydrides have been widely studied because they are potential materials for hydrogen storage, particularly for stationary applications. Such materials can be produced by high energy ball milling (HEBM) or severe plastic deformation (SPD) techniques, with proper activation (first hydrogenation) and H-absorption/desorption kinetics coupled to improved resistance to the air. Different preparation routes by the well-known technique of HEBM were used to produce powders with refined structures and H-absorption/desorption properties. Advanced techniques (high-pressure torsion, equal-channel angular pressing) and more traditional ones (for example, extensive cold rolling and cold forging) were studied to produce bulk samples with refined microstructures and controlled textures. By controlling processing parameters, HEBM or SPD techniques may furnish grain sizes ranging from the sub-micron to nanoscale, also enabling the introduction of a reasonable amount of dispersed additives and a high level of desirable (0001) type texture. This work it is examined the way processing by HEBM and SPD techniques can lead hydrogen storage materials to the following adequate aspects: fast kinetics (several interfaces: nano-grains and additives), facile activation (clean surfaces, interfaces, and favorable texture), and thermodynamic stability (alloying, cooperative interaction between phases and composites). The study suggests new and, in most cases, more accessible and cheaper options for producing hydrogen storage materials with satisfying hydrogen absorption/desorption kinetics and, considering composites, lowered hydride stability.

Keywords: hydrogen storage materials, magnesium-based hydrides, composite hydrides, severe plastic deformation, extensive plastic deformation

FERRITIC-INDUCED HIGH-ALLOYED STAINLESS STEEL PRODUCED BY LASER POWDER BED FUSION OF A DUPLEX STAINLESS STEEL

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Stainless steels are employed in harsh applications where corrosion and mechanical resistances are necessary. In the last few years, the production and use of these alloys by additive manufacturing have gained scientific attention due to the capability to manufacture near-net-shape components with complex geometries and controlled microstructure [1-2]. A high-alloyed ferritic-induced stainless steel was produced by laser powder bed fusion (L-PBF) using a duplex stainless-steel powder as a precursor, and its microstructure, wear and corrosion resistances were evaluated. Therefore, no heat treatment was applied to the ferritic-induced L-PBF stainless steel to restore the duplex structure. The L-PBF samples present high density and a high content of Cr, Mo, and N in solid solution (pitting resistance equivalent number, PREn, ~33), exhibiting a negligible corrosion current density of 10^{-7} A.cm^{-2}, with an enlarged passivation window ~ 1.2 V with respect to the corrosion potential, restraining the current density at the passivation plateau below 10^{-4} A.cm^{-2}. Therefore, regarding the corrosion resistance, the L-PBF specimen (ferritic microstructure) was comparable to its hot-rolled precursor (duplex microstructure). The L-PBF samples also presented a higher hardness value (290 HV0.5) and higher wear-resistance against sliding wear (specific wear rate of 5×10^{-4} mm^3·N^{-1}·m^{-1}) compared to its hot-rolled counterpart [3]. This work demonstrated that the ferritic-induced stainless steel from a DSS precursor was corrosion resistant in chloride-rich medium and wear resistant in sliding condition, being interesting to be used in as-built condition where corrosion and wear resistant are required.

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IMPACT OF ALLOYING AND HYDROGENATION OF Co-Zr BLENDS WITH DIFFERENT STOICHIOMETRY ON THEIR STRUCTURAL SPECTRAL AND CATALYTIC PROPERTIES

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Cobalt-zirconium alloys are widely used as hydrogen storage materials, active gas absorbers under high vacuum conditions, and magnetic materials. The properties of such alloys essentially depend on the phase and chemical composition, actual structure, defectiveness, and dispersity of particles. In this research work, X-ray diffraction, NMR, SEM, EDC methods were used to study the genesis of Co-Zr mixtures with the atomic ratio Co:Zr = 70:30, 53:47, 34:66 during mechanical activation (MA), hydrogenation, and incorporation into the Al_2O_3|Al matrix in the course of preparation catalysts for the Fischer-Tropsch synthesis (FTS). It was found that the initial powders of Co (grade PK-1u) and Zr (grade PCRK 1) are not phase homogeneous. After MA, small amounts of Co-Zr alloy are formed, as well as Co_3O_4 spinel. Oxidation of zirconium occurs and, at the same time, the formation of a hydride phase. It has been suggested that zirconium is oxidized by water used for protection against self-ignition, as well as hydrogenation of unoxidized zirconium by hydrogen formed during MA. Thus, a $ZrO_2/ZrH_x/Co$ nanocomposite is formed. After treatment in hydrogen at a pressure of 5.0 MPa, the phase composition of the nanocomposites did not change. However, in the ^{59}Co NMR spectra of the reduced samples, a line with a resonant frequency of about 216 MHz appeared, which is characteristic of single-domain particles (less than 70 nm in size) of metallic cobalt with fcc packing, the intensity of which is maximum for the sample with CoZr~1:1. It was found that this sample, after incorporation in an Al_2O_3/Al matrix, has the maximum activity in SPT and after testing contains a hexagonal cobalt phase, which is absent in other samples.

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EFFECT OF PRELIMINARY MECHANICAL ACTIVATION ON THE STRUCTURAL-PHASE STATE, THERMAL STABILITY, AND MICROHARDNESS OF Ni_3Al SAMPLES AFTER SPARK PLASMA SINTERING

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The influence of the duration of preliminary high-energy mechanical activation on the features of the structural-phase state and the level of microhardness of consolidated Ni_3Al samples obtained by spark plasma sintering has been studied. It has been established that the inhomogeneous structural-phase state of consolidated samples based on Ni_3Al in the case of preliminary mechanical activation of a short (1 minute) duration is a consequence of the formation of an inhomogeneous state of 3Ni-Al powder mixture precursor. An increase in the duration of mechanical activation, while providing a homogeneous phase composition, contributes to the refinement of the emerging grain structure and an increase in the microhardness values of the resulting Ni_3Al samples.

The main factors determining the processes of structural-phase transformation during the formation of Ni_3Al under the conditions of spark plasma sintering, depending on the preliminary mechanical activation duration, are revealed. It is shown that grain boundary strengthening is one of the effective mechanisms for increasing the strength of the material under study.

Using the methods of X-ray diffraction analysis, scanning and transmission electron microscopy, a comparative study of the features of the structural-phase state of Ni_3Al samples depending on the duration of preliminary high-energy mechanical activation and annealing temperature was carried out. Temperatures have been identified that provide simultaneous grain growth at a high nuclei density, which contributes to the formation of a fine-grained structural state. Depending on the state of the material, the corresponding microhardness values has been determined. The influence of the annealing temperature on the strengthening mechanisms has been analyzed.

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SYNTHESIS OF METAL MATRIX COMPOSITES BY SPARK PLASMA SINTERING

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Reactive spark plasma sintering (RSPS) is a sintering method that allows fast consolidation of powders and solid state synthesis of new phases during a single process stage. Metal matrix composites reinforced by ceramic particles can be formed in-situ using RSPS. The advantage of the in-situ approach is in the ability of synthesizing micro- and nanoparticles of unique morphologies during exothermic reactions. A matrix removes heat from the reaction zone. In addition, a matrix is a diffusion barrier for reagents. The synthesis of target phases in the presence of a metallic matrix during RSPS is affected by the components mutual chemistry [1].

In this work, RSPS of the Ti-C-3Cu, Ti-C-3Al and W-C-3Cu reaction mixtures was conducted. Prior to RSPS, the mixtures were mechanically milled using a high energy ball mill to form composite powder agglomerates. It was found that the synthesis of TiC reinforcement in the Ti-C-3Cu occurs due to the high solubility of titanium in a copper matrix. In the Ti-C-3Al system, the formation of strong $TiAl_3$ and Al_4C_3 phases prevents the synthesis of the desired TiC phase. For the reaction between tungsten and carbon in the W-C-3Cu system, a direct contact of these reactants is required, but the copper matrix acts as a diffusion barrier. During RSPS of Ti-C-3Cu and W-C-3Cu mixtures, the copper areas free from reinforcements can be formed owing to local melting by electrical current [2].

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INFLUENCE OF PLANETARY MILL OPERATING MODE AND GAS ATMOSPHERE ON THE MORPHOLOGY OF METAL POWDERS

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Mechanical alloying of metal powders is a promising method for producing high-entropy alloys. The kinetics of mutual dissolution of metals in planetary mills depends on many parameters, such as the rotation speed of the mill, the composition of the powder mixture, the gas atmosphere in the grinding jars, and others. In this work, the influence of the mode and operating time of the mill, as well as the gaseous atmosphere on the shape of powder particles, microstructure, crystal structure and purity (accumulation of iron and oxygen impurities) was studied. The mill rotation speed was varied from 300 to 694 rpm, the treatment time was from 5 to 90 minutes. Processing was carried out in four gas atmospheres: air, Ar, N_2, He. The studies were carried out on simple compositions - nickel powder (PNE-1) and an equiatomic mixture of Ni + Cu. The choice of these model compositions made it possible to reveal regularities that also operate in multicomponent mixtures of metal powders.

The results of the study showed that by choosing the operating mode of the mill and the gas atmosphere, it is possible to change the morphology and composition of the particles of metals and alloys over a wide range (Fig. 1).

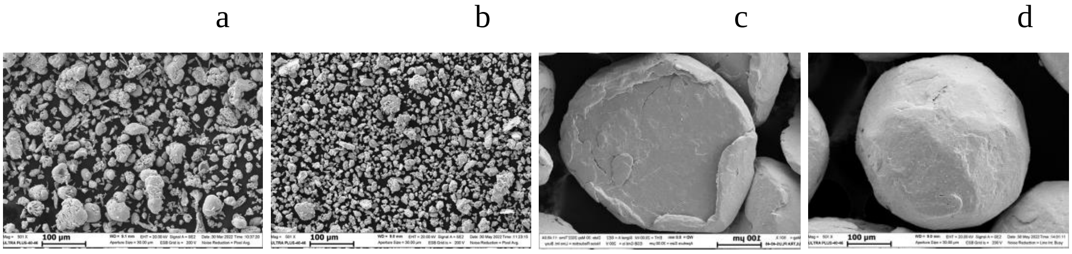

Fig. 1. Effect of a gaseous atmosphere on the morphology of Ni particles: initial powder (a), treatment in air (b), in argon (c), and in nitrogen (d). Processing mode for the (b), (c) and (d) cases was the same - 90 min at a speed of 694 rpm.

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COMPOSITES AND COATINGS BASED ON MECHANICALLY ALLOYDED MULTICOMPONENT PHASES

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A high fineness and homogeneous chemical composition of powders prepared by mechanical alloying make them good for producing compacted samples and applying coatings via various methods. Mechanical alloying and mechanochemical synthesis may significantly facilitate the formation of multicomponent phases of carbides and oxides, MAX phases, intermetallic compounds, quasicrystalline compounds, etc., or composites based on them [1–7].

In this study, we reports on composites based on multicomponent η-carbides $Nb_3(Fe,Al)_3C$, $(Nb,Fe)_6C$, $(W,Fe)_6C$ and $(W,Fe)_{12}C$, multicomponent phases based on intermetallic compounds $Nb_5Al_3C_x$, $Nb_5Si_3C_x$, and $Ti_5Si_3C_x$, as well as those based on G-phases in systems Ti-Ni-Si, Ti-Co-Si, Ti-Co-Al, and Ti-Fe-Al, as synthesized through mechanical alloying of respective elemental powders in organic liquid for the first time. Some of these multicomponent compounds have been prepared as monophases for the first time. Bulk composites based on $Ti_6Ni_{16}Si_7$ and $Ti_6Co_{16}Si_7$ were fabricated via magnetic pulse compacting, whereas composites based on $Nb_3(Fe,Al)_3C$ and Ti_2AlC were consolidated by spark plasma sintering. Coatings comprised of $(Nb,Fe)_6C$, $(W,Fe)_6C$ and $(W,Fe)_{12}C$ phases were applied to steel and iron via high-speed selective laser sintering. The properties of the as-prepared samples were characterized, including density, hardness, wear resistance, electrical resistance, electrocatalytic activity in the reaction of hydrogen evolution.

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THE ELECTROCHEMICAL CAPACITY OF HOLLANDITE $K_{1.6}(Ni_{0.8}Ti_{7.2})O_{16}$ INCREASING BY HIGH-ENERGY GRINDING WITH CARBON BLACK

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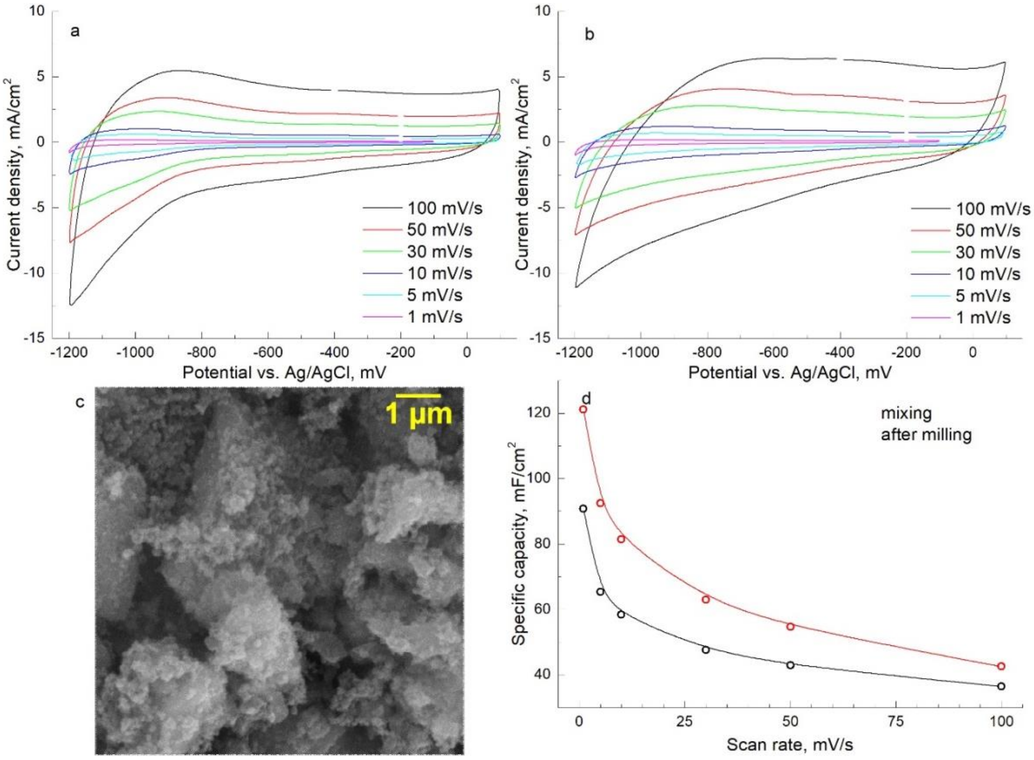
$K_{1.6}Ni_{0.8}Ti_{7.4}O_{16}$ with a hollandite structure (KNTO(H)) is synthesized by the solid-phase method. To reduce the contact resistance and to increase the specific capacitance, a conductive carbon coating its applied to the surface of the titanate obtained by joint grinding in a planetary mill for 3 hours. Electrochemical testing of electrodes with hollandite was done in a three-electrode cell against an Ag/AgCl electrode in 6M KOH electrolyte. Electrodes are tested current-voltage (CV) with potential from -1200 mV to 100 mV with subsequent calculation of the specific capacitance. It is found that the specific capacitance of an electrode with a carbon coating is 15–35% higher with low sweep rates (1 and 10 mV/s).



Electrochemical characteristics of the electrode based on KNTO(H).

CV of (a) KNTO(H) and (b) KNTO(H)/CB at different potential sweep rates. (c) SEM microphotographs of powders KFNO(H)/CB after joint grinding in a planetary mill for 3 hours. (d) The specific capacitance to the sweep rate of the potential of CV.

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INVESTIGATION OF ELECTRICAL CONDUCTIVITY OF MECHANICALLY ACTIVATED CLINOPTILOLITE ROCKS

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Mechanical activation makes it possible to change the physicochemical, including electrophysical, properties of natural zeolites in a way by varying the dose of the supplied mechanical energy. The amount of the energy dose (D, kJ/g) was calculated by the equation: $D = J \cdot t$, where J – energy intensity of the grinding apparatus, t – grinding duration, s. Mechanical activation of air-dry clinoptilolite-stilbite and clinoptilolite rocks with a zeolite content of at least 70% was carried out for 3, 5, 7 and 10 minutes in a vibratory attritor IVS-4 (D = 0.72; 1.20; 1.68; 2.40 kJ/g). The conductivity of tableted samples with a diameter of 16 mm and a thickness of 3-4 mm (dry pressing, press IP-1A-1000) was measured in the temperature range of 25÷100 °C using a teraohmmeter E6-13A ($\delta = 5\%$; constant current mode; U = 100 B; air humidity 26 %) and a three-electrode circuit. The porosity of the layer we determined by the experimental calculation method, using the values of the true and bulk densities found by pycnometric and gravimetric methods.

The porosity of the layer for powder samples ranges from 66 to 77% and increases with an increase in the supplied energy dose to 1.20-1.68 kJ/g. It was found that the specific electrical conductivity of mechanically activated clinoptilolite rocks at 25 °C is ~ 10^{-6}-10^{-9} Cm/ m, and at a temperature of 100 °C it increases by 1-2 orders of magnitude. It is calculated that the activation energy of the conductivity for the samples under study takes values from 0.16 to 0.72 eV with a confidence value of approximation of at least $R^2 = 0.9136$. It has been established that the dose of mechanical energy leading to the maximum increase in electrical conductivity is 1.20 and 2.40 kJ/g for clinoptilolite-stilbite and clinoptilolite rocks, respectively. The minimum electrical conductivity is observed in mechanically activated zeolite samples with a energy dose of 1.68 kJ/g. The highest conductivity value (3.7 10^{-6} S/m at 25 °C) has the sample of clinoptilolite-stilbite rock obtained from mineral powder mechanically activated for 5 minutes (D = 1.20 kJ/g).

MECHANOCHEMICAL SYNTHESIS AND DC ELECTRICAL CONDUCTIVITY OF PANI-BASED NANOCOMPOSITES WITH THERMOELECTRIC Te AND Bi_2Te_3 NANOPHASE

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Nowadays, one of the promising directions in the search for new high ZT thermoelectrics applicable in thermoelectric cells is the synthesis of paired organic-inorganic systems in the form of polymeric nanocomposites with p and n type electric conductivity. Their undisputed advantages are their high electrical conductivity combined with low thermal conductivity, light weight, mechanical flexibility as well as their high environmental friendliness and accessibility due to the variety of synthesis methods and the potential of modern chemical technology [1].

This paper presents the results of a mechanochemical synthesis of composites based on emeraldine salt of polyaniline (ES-PANI) and inorganic nanoparticles (Te^0 и Bi_2Te_3). The synthesis of ES-PANI/Te^0 and ES-PANI/Bi_2Te_3 nanocomposites was carried out by mixing ES-PANI and nanoparticles in the ratios of 1:20, 1:8 and 1:4 in a ball mill for 60 minutes. Te^0 and Bi_2Te_3 nanoparticles were pre-synthesized from powdered elemental tellurium in the basic reduction hydrazine hydrate-NaOH system, both as a result of oxidation of generated Te^{2-} anions and as a result of their interaction with Bi^{3+} ions [2]. The temperature dependence of the DC electrical conductivity of ES-PANI and the obtained nanocomposites was investigated in the temperature range of 25-80 ^oC using the Arrhenius and VRH models. The results show that the electrical conductivity values of ES-PANI and nanocomposites ($1.2 \leq \sigma_{DC} \leq 37.8$ mS/cm) as well as the specificity of its growth with increasing temperature indicate the semiconducting character of the conductivity in the investigated samples. The conductivity of the nanocomposites (9.3-3.5 mS/cm for ES-PANI/Te^0 and 4.2-1.2 for ES-PANI/Bi_2Te_3 at t=25 ^oC) decreased with a change in the ES-PANI/nanophase mass ratio from 1:4 to 1:20, indicating that a controllable change in the electrical conductivity of the nanocomposites by varying amount their inorganic nanophase is possible.

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INCREASED SINTERABILITY AND IONIC CONDUCTIVITY OF $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ AND $Na_3Zr_2Si_2PO_{12}$ SOLID ELECTROLYTES OBTAINED BY HIGH-ENERGY BALL MILLING

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Among well-known solid electrolytes (SE), the NASICON-structured $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) and $Na_3Zr_2Si_2PO_{12}$ (NZSP) have an ionic conductivity of about 10^{-4} - 10^{-3} S cm^{-1} at ambient temperature. Various sintering methods are used to obtain dense ceramics and increase grain boundary conductivity of SE, including microwave sintering, spark plasma sintering, hot pressing, cold sintering processes etc. In addition, liquid-phase sintering with fusible additives ($NaPO_3$, NaF, NaB_2O_4,) was proposed. However, these methods require using of expensive equipment and are difficult to scale-up.

One of the ways for increasing ionic conductivity of SE is high-energy ball milling (HEBM). It is known that HEBM leads to dispergation, amorphization, formation of defects, various structural transformations in solids, and chemical reactions. In this work, we studied the effect of HEBM on the conductive properties of LATP and NZSP. It is shown that HEBM is an alternative method of increasing sinterability and ionic conductivity of SE to 2.51 g·cm^{-3} and $1.20 \cdot 10^{-4}$ S·cm^{-1} for LATP and 3.14 g·cm^{-3} and $2.13 \cdot 10^{-3}$ S·cm^{-1} for NZSP.

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FAST SOLID-STATE REACTION WITH THE FORMATION OF $NA_3V_2^{3+}(PO_4)_2F_3$ CATHODE MATERIAL ASSISTED BY THE MECHANICAL ACTIVATION

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Among the known cathode materials for sodium-ion batteries, a family of sodium-vanadium fluoride phosphates with the $Na_3V_2O_x(PO_4)_2F_{3-x}$ ($0 \leq x \leq 2$) general formula is believed to be one of the most promising ones. The oxidation state of vanadium in these compounds ranges from +3 to +4 and affects the Na-(de)intercalation mechanism and operating potential. $Na_3V_2^{3+}(PO_4)_2F_3$ end member shows the highest potential of 3.9 V *vs.* Na^+/Na. Although the solid-state reaction between NaF and VPO_4 is widely used to produce $Na_3V_2(PO_4)_2F_3$, its mechanism and kinetics have not been studied yet.

In this work, we investigated the effect of preliminary high-energy ball milling (HEBM) on the reaction using *in situ* high-temperature time-resolved synchrotron and laboratory powder X-ray diffraction, *in situ* transmission electron microscopy, differential scanning calorimetry, and infrared absorption spectroscopy were used.

It was found that during high-temperature heat treatment, VF_3 is release into the gas phase, which leads to the formation of the $Na_3V_2(PO_4)_3$ admixture. To overcome this drawback, it is necessary to use the mixture of reagents in the form of pellets, so that the evolution of VF_3 becomes difficult and pure $Na_3V_2(PO_4)_2F_3$ is formed. The reaction was attributed to a “dimensional reduction” formalism; it proceeds quickly with the unilateral diffusion of Na^+ and F^- ions into VPO_4 particles, which is a limiting stage. The use of HEBM leads to the mechanism corresponding to the third-order reaction model and significantly accelerates the interaction so that it is completed in 40 seconds at 570 ^oC. When HEBM is used, the rate constant increases from 3.5×10^{-5} to 3.4×10^{-3} s^{-1}, and the diffusion coefficient increases from 2×10^{-14} to 4×10^{-13} cm^2 s^{-1}. The calculated apparent activation energy is $\sim$290 kJ mol^{-1}. The electrochemical properties of the as-prepared $Na_3V_2(PO_4)_2F_3$ are not inferior to the properties of the materials prepared by conventional solid-state synthesis.

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FREE VOLUME IN MECHANOCHEMICAL NANOPOWDERS OF COMPLEX OXIDES WITH PEROVSKITE, FLUORITE AND SPINEL STRUCTURES

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The use of mechanochemical technology is most promising in inorganic materials science, especially when creating composite functional materials. This direction is most compatible with the technical capabilities of high-energy mills. In addition, the creation of nanocomposites with oxide and other ceramics by mechanical activation has decisive advantages over other methods. Like all methods in materials science, the mechanochemical approach has its advantages, features and disadvantages. The obvious problem of material contamination was solved long ago. The inhomogeneity of MA materials and the wide distribution of aggregate sizes can be eliminated by wet grinding or separation of nanopowders using Electromassclassifier technique. However, all powders of mechanochemical origin have a specific feature - a huge content of vacancy defects - a free volume that can reach 10% according to the theory of ultrafast mechanosynthesis of complex oxides. As studies of various materials have shown, the free volume has a negative impact on the functional properties. The report will demonstrate the results of structural studies of complex oxides with the structure of perovskite, fluorite and spinel, which are most used in materials science. Direct measurements of the density by He-pycnometry in MA perovskite $BaTiO_3$ as an example showed a free volume of 9.1%. Studies of the MA of perovskites by Mössbauer spectroscopy gave a value of 9% in terms of the content of 5-coordinated Fe^{3+} ions. The study of complex oxides with the fluorite structure indirectly showed the presence of free volume from the change in the lattice parameter during annealing. Metastable fluorite δ-Bi_2O_3 has a maximum potential in oxygen membranes, but undergoes accelerated phase degradation in the presence of free volume, which promotes the formation of nuclei of stable phases. In the case of spinel, annealing of the free volume is observed indirectly via a decrease in the lattice parameter. Direct evidence for the fixation of Fe^{3+} states, equivalent to the formation of a free volume, was also obtained by Mössbauer spectroscopy. To date, the application of MA in membrane science with long-term applications is most useful due to the acceleration of hidden or slow degradation processes.

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MECHANICAL PROPERTIES OF REFRACTORY HIGH ENTROPY ALLOYS

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High Entropy Alloys (HEAs) is a new class of metastable materials that currently receives increasing scientific and technological attention. Unlike conventional metallic alloys, which are based on one (rarely two) main elements, HEAs are multiple-principal element alloys, considerably extending the alloy design horizons compared to conventional approaches. These alloys often consist of single or dual phase microstructures with simple crystal structures such as BCC or FCC, contrary to the conventional metallurgical wisdom dictating the formation of a number of intermetallic phases. HEAs with promising properties, including high strength, good wear characteristics, excellent corrosion resistance and good engineering performance at high temperatures are very attractive for a wide variety of industrial applications. Here we discuss on the mechanical behaviour of HEAs, focusing on alloys mainly consisting of refractory elements, and we uncover relations between their structure and properties.

MECHANOACTIVATED SYNTHESIS OF NICKEL-ALUMINATE SPINEL

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It is known that spinel formation requires high temperatures. To activate precursors participating in solid-state reaction it is possible using a mechanochemical pretreatment. The effect of preliminary mechanical activation by mainly impact (planetary mill, PM) and attrition (ball-ring mill, BRM) as well as a microwave treatment for the nickel-aluminate spinel ($NiAl_2O_4$) was studied.

Oxides, hydroxides, and salts (nitrates) of Ni and Al were chosen to compare the precursors reactivity. The $NiAl_2O_4$ yield values for different precursor combinations and various pretreatment modes of reaction mixtures before the burning are compared in Table.

Table. $NiAl_2O_4$ yield (%) after the burning (900 ^oC) from mixtures pretreated by microwave and mechanical methods

Precursors	With no treatment	After treatment		
		in magnetron oven	in BRM	in PM
$Ni(OH)_2 + Al(OH)_3$ (gibbsite)	45 ± 5	50 ± 6	54 ± 6	78 ± 6
$Ni(OH)_2 + Al(OH)_3$ (bayerite)	51 ± 3	56 ± 4	58 ± 5	81 ± 5
$Ni(OH)_2 + AlOOH$ (boehmite)	49 ± 4	49 ± 4	54 ± 5	80 ± 6
$Ni(OH)_2 + Al(NO_3)_3$	49 ± 6	66 ± 5	59 ± 5	84 ± 5
$Ni(NO_3)_2 + Al(OH)_3$ (gibbsite)	44 ± 4	71 ± 8	61 ± 7	86 ± 7
$Ni(NO_3)_2 + Al(OH)_3$ (bayerite)	50 ± 3	76 ± 8	66 ± 5	89 ± 5
$Ni(NO_3)_2 + AlOOH$ (boehmite)	47 ± 5	69 ± 6	63 ± 6	87 ± 6
$Ni(NO_3)_2 + Al(NO_3)_3$	54 ± 6	99 ± 3	81 ± 9	100 ± 6

The combined method consisted of a mechanical treatment of Ni and Al nitrates mixture in a planetary mill and the subsequent burning in a thermal oven was considered as the most effective because it resulted in the practically single product. The microwave treatment took up an intermediate position by the effectiveness. The maximum yield was under using nickel and aluminum nitrates as precursors.

Structural characteristics, UV-visible and FTIR spectra, specific surface area, and pore size of $NiAl_2O_4$ were analyzed.

MECHANICAL ACTIVATION OF DOUBLE COMPLEX SALT $[Cr(ur)_6][Fe(C_2O_4)_3]\cdot 4H_2O$

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By means of mechanical activation (MA), it is possible to obtain nanocrystalline systems with different structural and phase composition, dispersity and thermal and magnetic properties. Chemistry of double complex salts (DCS) is currently being actively developed. However, the literature on the effect of MA on the physicochemical properties of complex salts is scarce. Such studies have not been carried out for DCS previously.

The goal is to study the effect of MA on the thermolysis of $[Cr(ur)_6][Fe(C_2O_4)_3]\cdot 4H_2O$ (ur – $CO(NH_2)_2$). The product of thermolysis in air at 900^oC of this DCS is $(Fe,Cr)_2O_3$. Mixed oxide of Cr and Fe can be used as effective catalyst for the purification of exhaust gases from NO_x. Since pre-MA can reduce the temperature of the subsequent thermal treatment of the DCS, an attempt has been made to obtain such a mixed oxide at lower temperatures.

The IR spectra for the samples subjected to 10 and 20 h of MA coincided. The total number and intensity of peaks decreased for the spectra of samples after MA. The $C_2O_4^{2-}$ was changed the most. Peaks corresponding to urea vibrations did not change. The partial destruction of the structure of the anion sphere occurred. Samples after 10 h of MA with a ratio of spheres of 20:1 and 10:1 are X-ray amorphous. The STA showed that MA for 10 h reduces the temperature of the end of thermolysis (the beginning of the exit of the TG to a plateau) by 80 ^oC, and if it acts for 20 h, then the temperature reduces by 100 ^oC compared to the non-activated DCS. The product of thermolysis of a DCS at 550°C without MA is a mixture of oxides based on Fe_2O_3 (sample **I**). Samples products of thermolysis at 550°C with MA exposed for 10 h and 20 h (samples **II** and **III**, respectively) are mixtures of hematite and eskolaite. All 3 samples have the same specific atomic volume = 48.9 $Å^3$. The crystallite size D of **I** is 18.0(3.0) nm; and Fe_2O_3 has D 31.5(4.5) nm for **II** and **III**; Cr_2O_3 has D 17.5(3.5) nm. Prolonged MA probably led to the aggregation of the formed Fe_2O_3. MA affected the course of further thermolysis of DCS and lowered the final temperature of thermolysis. This approach did not vastly reduce the temperature of obtaining the $(Fe,Cr)_2O_3$.

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EFFECT OF SHORT-TERM PRELIMINARY MECHANICAL ACTIVATION OF EUDIALYTE CONCENTRATE ON EXTRACTION LEACHING OF REM

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Extraction leaching of eudialyte concentrate allows to suppress the process of gelation of silicic acid.

Investigation of the effect of extraction leaching of eudialyte concentrate (49.92 % SiO_2, 14.05 % Na_2O, 9,81 % ZrO_2, 1.84 % REM_2O_3) 100% TBP saturated with concentrated HNO_3 (TBP-HNO_3 system) and HCl (TBP-HCl system) showed that without mechanical activation (MA) in 1 hour at t = 50 ^oC and the ratio of concentrate to the organic phase C:O=1:10 extraction of REM into the organic phase was 3.28 and 55.85%, respectively.

Preliminary mechanical activation (in LAIR-0.015) at the ratio of the mass of the balls to the concentrate (Mb:Mc) 800:40, acceleration of 25 g for 60 seconds ensures the extraction of REM from the eudialyte phase into the organic phase of the TBP-HNO_3 and TBP-HCl systems, all other conditions being equal, 6.18 and 99.99%, respectively.

The effect of the duration of MA and the energy of structural changes (total ΔE_Σ and stored in the form of a freshly formed surface of the coherent scattering region ΔE_S, determined according to X-ray diffraction analysis using the methodology for assessing the energy state of the crystal lattice of activated material [1]) on the extraction of REM from the eudialyte phase into the organic phase of the TBP-HCl system is shown in Fig.1. The correlation of REM extraction with both ΔE_Σ and ΔE_S has been established.

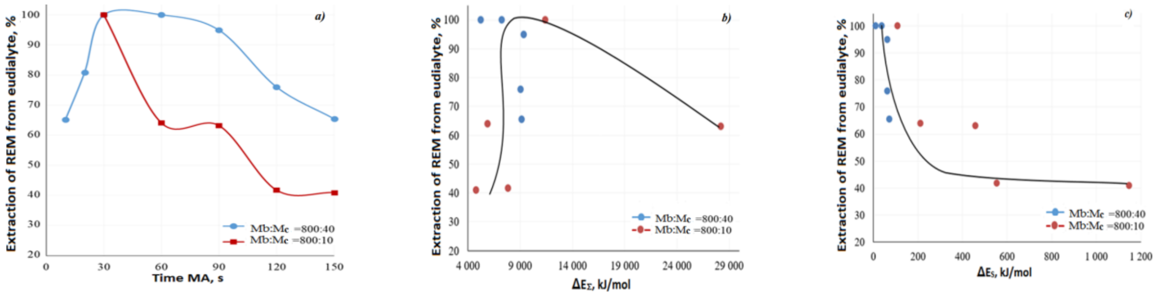

Fig. 1. The effect of the duration of MA (*a*) and the energy of structural changes (ΔE_Σ (*b*), ΔE_S (*c*)) on the extraction of REM from the eudialyte phase into the organic phase of the TBP-HCl system (t = 50 ^oC, C:O=1:10, τ=1 h).

The values of energy characteristics ΔE_Σ and ΔE_S can be used as criteria for optimizing the process of extraction leaching of eudialyte concentrate.

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GRINDING THE COMPONENTS OF A MINERAL MIXTURE IN A HIGH-ENERGY PLANETARY BALL MILL

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A mixture corresponding to the mineralogical composition (according to calculation) wt.% was used as the starting material: titanite - 57.5; apatite - 8.0; nepheline - 9.5; aegirine - 25.0. The powder mixture was thoroughly mixed before the start of the experiments in a Turbula mixer. The mixture of powders in the required amount was loaded into 45 ml hardened chromium steel mill vials along with 22 balls (diameter 10 mm). The ratio of the masses of balls and powder loading (B: P) changed in the following options: 5:1; 10:1; 15:1; 20:1. The experiments were carried out on a planetary mill Fritsch GmbH Pulverisette-7 at different rotation speeds for each of the options B: P: 300, 500 and 700 rpm. For each combination of ratio (B: P) and rotation speed, three durations of the high-energy ball grinding were used: 30, 60, and 90 minutes.

Conclusions based on the results of the experiments and recommendations:

- Of the controlled parameters of the process (speed, rotation, time and the ratio of the mass of balls to the mass of the powder), the ratio B: P has the greatest influence;
- With the introduction of maximum energy values to the crushed material in the time interval from 60 to 90 minutes, the decrease in particle size stops and agglomeration into larger particles begins, accompanied by a decrease in the specific surface area of the particles;
- the size of crystallites was calculated by the Scherrer method, and the microstress indicators were determined by the Williamson-Hall method;
- Further studies of the system under study should include studies associated with the analysis of the dynamics of the distribution of the elements that make up the mixture in order to determine the influence of the process parameters on it. One of the possible methods may be the method using the QBSD detector in combination with SEM analysis.

MECHANICAL ACTIVATION OF CARBON MATERIALS: GRAPHITE, CARBON BLACK, CARBONIZED ASPHALT

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Mechanical activation (MA) is environmentally friendly and efficient methods for preparing nanomaterials with new functional properties. MA of various carbon materials was carried out: graphite, carbon black (CB) and carbonized asphalt, which is a heavy oil residue. Mechanical activation of carbon materials was performed in air using a water-cooled planetary mill AGO-2 (Novits Ltd., Novosibirsk, Russia) at 100 g acceleration of milling bodies and activation time of 1–60 min. Mechanical activation time was varied from 1 to 60 min. All mechanically activated samples were studied using physicochemical research methods: X-ray diffraction analysis, IR and Raman spectroscopy, transmission electron microscopy (TEM) and low-temperature nitrogen adsorption.

MA of graphite leads to the destruction of crystallites and decrease of the number of the layers in the graphite stack. Turbostratic disordering occurs with increasing graphite processing time. The graphene layers are randomly displaced parallel to the basal plane. The relations of the specific surface area and pore volume on the activation time are extreme with maxima of 460 m^2/g and 0.43 cm^3/g, respectively.

MA of CB causes destruction of agglomerates and changes in its porous structure. The number of large pores with sizes > 50 nm decreases and small pores with sizes of 3–5 nm appear. TEM images of activated CB show an order in the mutual arrangement of graphene layers, which is not typical for the structure of the initial CB samples. Thus, the obtained results reveal that after MA it is possible to rearrange the graphene layers in the CB globules.

Asphalt is a by-product of oil refining. But the carbon content of asphalt is more than 85%, which makes it an excellent raw material for the production of carbon materials. Carbonization of asphalt and its further MA with alkali (KOH) and heat treatment in Ar at 750ºC leads to the formation of microporous carbon materials with the following textural characteristics: S_{BET}=2935 m^2/g, $V_{\sum}$=1.57 cm^3/g, V_{micro}=1.0 cm^3/g. The textural parameters of the carbon material obtained by a similar technology, but without the stage of mechanical activation, are much lower: S_{BET}=1997 m^2/g, $V_{\sum}$=0.88 cm^3/g, V_{micro}=0.73 cm^3/g.

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MECHANOCHEMICAL SYNTHESIS OF TITANOPHENYLSILOXANES

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In this work, we studied the mechanochemical interaction of polyphenylsilsesquioxane with titanium(IV) oxide, bis-(acetylacetonate) titanium dichloride, bis-(benzoylacetonate) titanium dichloride, and bis-(dibenzoylmethanate) titanium dichloride. We have studied some reaction products as a precursor for wollastonite ceramics, also got by solid-phase synthesis based on natural renewable raw materials.

We have established that with an increase in the volume of the organic ligand at the titanium atom, metal incorporation into the polymeric siloxane chain decreases. We show that, under conditions of mechanochemical activation, titanium b-diketonate complexes form their own polymeric products, and the yield of the polymerized complex increases with an increase in the ligand's volume. This process prevents the entry of titanium atoms into the polymeric siloxane chain.

It is shown that when titanium compounds are introduced into wollastonite ceramics, the porosity decreases and the material is strengthened. The maximum decrease in porosity was observed when wollastonite was modified with a polymerized titanium acetylacetonate complex. We have shown that ceramics modified with the compounds got are not capable of ceasing the formation of the *Pseudomonas aeruginosa* bacterial film. Thus, these additives are not toxic.

Because of high-temperature processing of polytitanphenylsiloxanes, titanosilicate nanocomposites are got, which are used as oxidation catalysts, which can later replace expensive platinum and palladium catalysts used in the automotive industry. The group character of organic substituents at silicon and titanium atoms, which disappears during heat treatment, can be used for the synthesis of homogeneous materials. The relatively high UV resistance and high hydrophobicity of the resulting polymers are used to create protective coatings.

PHYSICOCHEMICAL AND CATALYTIC PROPERTIES OF THE Pt/TiO$_2$ CATALYST FOR CO OXIDATION BASED ON DEFECTIVE TiO$_2$, OBTAINED BY CENTRIFUGAL THERMAL ACTIVATION TECHNOLOGY AND MODIFIED WITH IRON OXIDE

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The technology called centrifugal thermal activation (CTA) of powdered materials developed in [1, 2] was used to modify the structural and textural parameters of TiO$_2$ with anatase structure. The heating rate of particles of the processed materials can exceed 1000 °C/sec, which has a significant effect on the formation of the phase composition, microstructure and texture of the CTA products. It was found that the crystal structure of the anatase phase formed below 650 °C is quite defective. TiO$_2$ obtained above 300 °C characterized a much higher specific surface area and a finely porous structure in comparison with the samples obtained traditional synthesis methods.

Supported Pt/TiO$_2$ catalysts are active in low-temperature CO oxidation. To obtain a wider range of defective TiO$_2$ oxide materials used as support in these type catalysts has significant interest. In order to increase activity, catalysts are often modified with oxides of transition elements, among which iron oxide is one of the most promising.

Catalysts 1 wt. % Pt/TiO$_2$ and 1 wt. % Pt/(1–10 wt % Fe$_2$O$_3$–99–90 wt % TiO$_2$) were prepared by impregnating anatase of TiO$_2$ with an aqueous solution of iron nitrate to the moisture capacity, followed by impregnation with an aqueous solution of platinum nitrate, drying, and heat treatment in air at 500 °C.

The modification of the Pt/TiO$_2$ catalyst based on CTA TiO$_2$ anatase phase with the addition of iron oxide on the formation of the microstructure, the electronic state of platinum, and their effect on the catalytic properties in the CO oxidation reaction was studied.

This work was supported by the Ministry of Science and Higher Education within the Government task of Boreskov Institute of Catalysis (project AAAA-A21-121011390054-1).

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LAYERED Sr_2TiO_4 PREPARED USING MECHANOCHEMICAL ACTIVATION OF DIFFERENT INITIAL COMPOUNDS: GENESIS, STRUCTURAL AND CATALYTIC PROPERTIES

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Layered Ruddlesden-Popper $A_{n+1}B_nO_{3n+1}$ perovskites have a wide range of applications such as magnetic materials, high-temperature superconductors, photo- and heterogeneous catalysts. Layered perovskite-like Sr_2TiO_4 is considered as a promising catalyst for oxidative coupling of methane (OCM) – a potential direct route to produce C2 hydrocarbons. In this work, Sr_2TiO_4 samples were synthesized using mechanochemical activation (MA) of the mixtures containing $SrCO_3$ or SrO and TiO_2 or $TiO(OH)_2$ with subsequent annealing at 900 and 1100°C. The influence of the raw materials and MA conditions on formation of Sr_2TiO_4, its structural and catalytic properties in OCM was studied. According to FT-IRS and XRD data, MA leads to the disordering of the starting components and formation of $SrTiO_3$ only in the mixtures with SrO that was more pronounced when using the amorphous $TiO(OH)_2$ containing a lot of OH-groups or the high-power ball mill AGO-2. Sr_2TiO_4 is formed in all samples after annealing at 900°C but its amount was considerably different in the line with the peculiarities of MA products. Sr_2TiO_4 was mainly contained in the case of $SrCO_3$ or SrO and $TiO(OH)_2$ compared to the mixtures with TiO_2. The single phase Sr_2TiO_4 was only obtained from MA products containing $SrCO_3$ after annealing at 1100°C and it was found that this sample had structural defects. The FE-SEM micrographs have shown that the sample synthesized from the $SrCO_3$+TiO_2 comprised of the plates with the thickness of ~ 50 nm along with the well crystallized particles of ~500 nm while all other samples contained only three-dimensional particles of 200-1000 nm. The maximal CH_4 conversion and C2 yield (25.6 and 15.5% at 900°C, respectively), the high long-term stability was observed for the sample obtained from ($SrCO_3$+TiO_2) showing structural defects, the specific surface morphology and optimal values of the surface Sr concentration and O_o/O_p ratio.

This research was carried out within a State Assignment to the Boreskov Institute of Catalysis SB RAS (project No. AAAA-A21-121011490008-3).

SYNTHESIS OF MONOPHASIC LEAD INDIUM TANTALATE $PbIn_{1/2}Ta_{1/2}O_3$ WITH PEROVSKITE STRUCTURE

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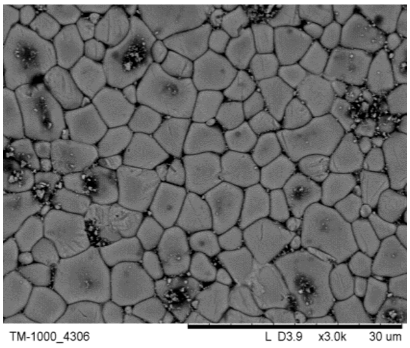
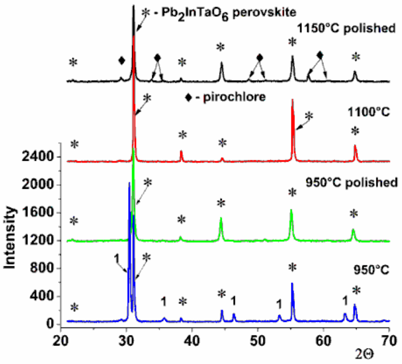
Piezoceramics are widely used in transport, energy, space and laser technology, microelectronics and optical instruments. Obtaining monophasic perovskites is extremely important because the presence of the pyrochlore phase in the ceramic significantly reduces its technical characteristics. Perovskite $PbIn_{1/2}Ta_{1/2}O_3$ is a promising basis for creating ceramic capacitor, piezoelectric, pyroelectric and posistor materials.

The aim of this study is to obtain monophasic $PbIn_{1/2}Ta_{1/2}O_3$ with a perovskite structure using mechanochemical synthesis and subsequent sintering in volumes that allow producing the samples suitable for making the products used in industry.

At the moment only two methods for obtaining the perovskite phase are known from the literature. The first one is to get a thin film sample 0.15 mm thick and 4 mm in diameter. The second one is to obtain from the melt a mixture of pyrochlore and perovskite phases of small (0.3 × 0.3 × 0.2 mm) crystals that require additional microscopic sorting according to the types of phases. Note that it is absolutely unclear how to make a product for industrial use from these crystals and whether the perovskite structure will be preserved in this case.

In this paper we consider a number of methods the use of which yields the perovskite phase. It is shown that such a phase has been obtained. The figures show diffraction patterns confirming the presence of the perovskite structure and a photo of the resulting structure.





A patent for the invention No. 2736947 has been obtained based on the results of these studies.

INVESTIGATION OF AN EXTENSIVE DIFFUSIVE ZONE FORMATED BY BORIDING IN AN INDUCTION FURNACE

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The report presents the results of studies of the diffuse zone formed as a result of boriding steel 20 at 1000 °C in an induction furnace for 5, 10 and 15 minutes. On the end surface of cylindrical samples of steel 20, a coating was applied containing a mixture of: Fe-25% + H_3BO_3-75%, an inert additive Na_2SiO_3, activators – NH_4OH, C. The results of studies of 4 samples are presented. In the coating of samples 1 and 3, liquid glass was present; in samples 2 and 4, there was no inert additive.

The main phases obtained in the experiments are FeB, Fe_2B and B, which formed composites with a hardness of 2837, 2862, 2362, 2604 MPa. The study of the microstructure showed that the layers consist of two phases of borides and the St20 matrix: the FeB phase turns brown, and Fe_2B turns yellow, and boron crystals are white. A porous zone about 50 μm in size is formed. Obtained values of boron diffusion coefficient: sample 1 – $1.35\cdot10^{-9}$ m^2/s, sample 2 – $1.6\cdot10^{-9}$ m^2/s, sample 3 – $0.675\cdot10^{-9}$ m^2/s, sample 4 – $0.242\cdot10^{-9}$ m^2/s, which is two orders of magnitude higher than the values of the boron diffusion coefficient given in the literature – $1.82\cdot10^{-11}$ m^2/s.

It has been established that an extensive diffusion zone during boriding in an induction furnace by heating at a temperature of 1000 °C is already formed within 5 minutes, and the resulting iron borides are chemical compounds of FeB and Fe_2B. The presence of an inert component of Na_2SiO_3 in the mixture leads to the formation of a porous structure of the borated layer, and the absence of an inert component in the composition of the mixture reduces the thickness of the boride layer and leads to the disappearance of pores.

MECHANICAL AND TRIBOLOGICAL PROPERTIES OF CoCrCuxFeNi HIGH ENTROPY ALLOYS, MANUFACTURED BY MECHANICAL ALLOYING AND HOT PRESSING

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A new alloy concept, named high-entropy alloy (HEA) or multicomponent alloy, is widespread in researches of materials with good combination of strength and plasticity, especially in CoCrFeNi based system. Various researches in CoCrFeMnNi, CoCrFeNiTi, CoCrFeNiV and other related HEAs demonstrated high potential of this approach. Copper appears to be a proper additive for improvement of CoCrFeNi HEAs, as it exhibits similar mechanical and physical properties. Nevertheless, recent works dedicated to studying of CoCrCuFeNi HEAs, produced by melting techniques, showed questionable results on mechanical properties. The possible reason of their mediocre mechanical properties is microstructure inhomogenueity, caused by low copper solubility in Fe, Co, Cr and dendritic segregation during crystallization.

A promising solution to the problem of CoCrCuFeNi HEAs manufacturing with a combination of high mechanical properties is the formation of other types of microstructure. It can be realized through the application of alternative technologies, for example, based on powder metallurgy. Due to the use of mechanical alloying (ML) and hot pressing (HP) methods, it is possible to obtain alloys with a nanocrystalline structure and high homogenueity, despite significant limitations in the solubility of the components.

In this work, CoCrCuFeNi HEA powders were obtained from elemental metal powders using an «Activator-2s» planetary ball mill. Their consolidation was carried out by the HP method at temperatures 950–1100°C. The copper concentration in the alloys was varied in the range of 0–20 at.%. It was found that HEAs with a copper content of less than 9 at.% are single-phase and contain only a solid solution with a face-centered cubic crystal lattice. At a copper concentration of 10-20 at.% a secondary phase precipitates, which is similar in chemical composition and type of structure to copper. The maximum tensile strength and hardness is shown by the alloy $CoCrCu_{0.5}FeNi$ (10 at. % Cu) – 1070 MPa. The high mechanical properties can be attributed to the solid solution hardening of the matrix and the dispersed nature of the precipitates of the secondary copper phase.

This work was carried out with financial support from the Russian Science Foundation (Project No. 22-79-10144).

STRUCTURE FORMATION DURING EXPLOSION WELDING OF COPPER AND MOLYBDENUM

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The study of the properties of composites and the physico-chemical processes occurring in them during explosion welding makes it possible to obtain materials with unique properties, which opens up new opportunities for solving urgent problems [1, 2]. The aim of the work: the study using the cluster approach of structural–phase transformations occurring during joint plastic deformation in the copper-molybdenum system.

Composite material samples were obtained by explosion welding of a multilayer package of copper and molybdenum plates, as well as by pressing molybdenum wire into copper on a hydraulic press. It is shown that in the process of plastic deformation, structures of the type of solid solutions were formed in the contact zone of the components. When deciphering X-ray diffraction patterns, atomically ordered (superstructural) solid solutions based on both copper and molybdenum were found. In addition, phases with an icosahedral structure have been identified.

Thus, the nonequilibrium conditions for obtaining the composite material provoked the occurrence of nonequilibrium phases. It is shown that, depending on the interaction energy, either solid solutions based on the lattices of the initial components or solid solutions with an icosahedral structure obtained an advantage.

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INFLUENCE OF MECHANICAL ACTIVATION MODES ON THE FORMATION OF VKNA ALLOY

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Improving the performance properties of high-temperature materials based on nickel aluminides remains one of the urgent problems of materials science [1,2]. A special feature of this study is the introduction of alloying elements into the powder mixture of nickel and aluminum that correspond to the composition of the Ni_3Al-based superalloy (VKNA), and mechanical activation (MA). The obtained mechanocomposites will later be used for spark plasma sintering (SPS) [2].

Mechanical activation of nickel, aluminum, and alloying element powders was performed in the planetary ball mill AGO-2. Reactants were activated in three modes of mill operation, which differ in mechanical activation time (1, 3, and 5 minutes). The modes were chosen for the following reasons: when the MA was carried out for less than 1 minute, there was no uniform mixing of the components, and over 5 minutes there was significant rubbing with grinding materials. Thus, based on the conducted studies, the optimal MA mode for forming the most uniform fine-grained structure of sintered materials of the VKNA composition is determined: the MA time is 3 minutes; the working medium is argon; the centrifugal acceleration of the balls is 40g.

This study was funded according to Russian Science Foundation research project № 21-79-00154, https://rscf.ru/project/21-79-00154. Research was conducted at core facility «Structure, mechanical and physical properties of materials».

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STUDY OF THE KINETICS OF AUSTENITE DECAY UNDER ISOTHERMAL CONDITIONS WITH MICROALLOYING WITH TITANIUM

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Due to the achievement of a wide range of technological and service properties, such as high strength, toughness, ductility and high corrosion resistance, new microalloyed materials have found wide application in the railway, engineering and other areas of modern industry. The authors of the work suggest that mechanical grinding of microalloyed material makes it possible to obtain a powder whose particles will inherit the properties and structure of the original material. The resulting powders will be in demand by thermal spraying and laser cladding to create functional surfaces.

Studies of the patterns of influence on the structure of microalloying elements at the stage of crystallization due to the influence on the kinetics and morphology of the process were analyzed in works [1,2]. At the moment, the formation of a fine structure by means of transmission electron microscopy has not been fully studied.

This paper considers the use of titanium as a microalloying additive to carbon steel. The addition of titanium makes it possible to form nitrides, carbides and carbonitrides. It should be noted that when high temperatures are reached, nitrides make it possible to control the grain size of austenite during heating before hot deformation, as well as during welding, especially in the heat-affected zone.

After heat treatment, the metal matrix of the alloy consists of hidden lamellar and coorbital perlite with the inclusion of a second phase. A feature of microalloyed alloys is the content of widmanstatt type ferrite in the intergranular space and in the bulk of the grain. It has been established that the lath structure of pearlite is lost, while pearlite ferrite contains a small number of dislocations due to the separation of the second phase.

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APPLICATION OF FERROTITANIUM FOR TiC-Fe METAL MATRIX COMPOSITES PRODUCTION

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«TiC+Fe» metal matrix composites (MMC) are known in the form of sintered materials (carbide steels) and powders for composite coatings surfacing. MMC powders are produced by self-propagating high temperature synthesis (SHS) method in reaction mixtures of titanium, carbon and iron or its alloys. The iron concentration in the mixtures does not exceed 60 vol.%, which is not enough to ensure the weldability of the synthesized composite powder.

It is common, that preliminary mechanical activation (MA) of reaction mixtures can results in lower ignition temperature and higher contents of thermally inert additives in the reaction mixtures. However, our attempts to apply MA to the “Ti+C+high-speed steel” and “Ti+C+high-chromium cast iron” mixtures failed due to the blocking of the titanium-carbon reaction surface with Fe-alloy.

It is prospective to substitute titanium and iron in reaction mixtures by ferrotitanium alloy, which is produced in an industrial scale and is ten times chipper of the titanium powders. The FeTi35C5 ferroalloy contains 84 vol.% Fe_2Ti and 16 vol.% Ti_5Si_3.

Investigation results of the synthesis in MA mixtures of FeTi35C5 ferrotitanium powder (<56 μm) with 7.5 wt.% carbon black (0.3-0.2 μm) are summarized in the present work. The MA of the mixtures was carried out on planetary ball mill « Activator-2S». The synthesis products were obtained by two modes: self-propagating wave combustion mode (SHS) and thermal explosion (TE) while heating up to 500 °C.

Phase composition of the SHS products depends of the MA duration. The most TiC content in the synthesis products was obtained after 10 and 15 minutes MA duration. The phase composition of TE products after one hour at 500 ^{o}C does not depend on the MA duration. TE product consists of TiC and 50 vol % α-Fe alloy.

MECHANOCHEMICAL SYNTHESIS OF Pd(II) PINCER COMPLEXES

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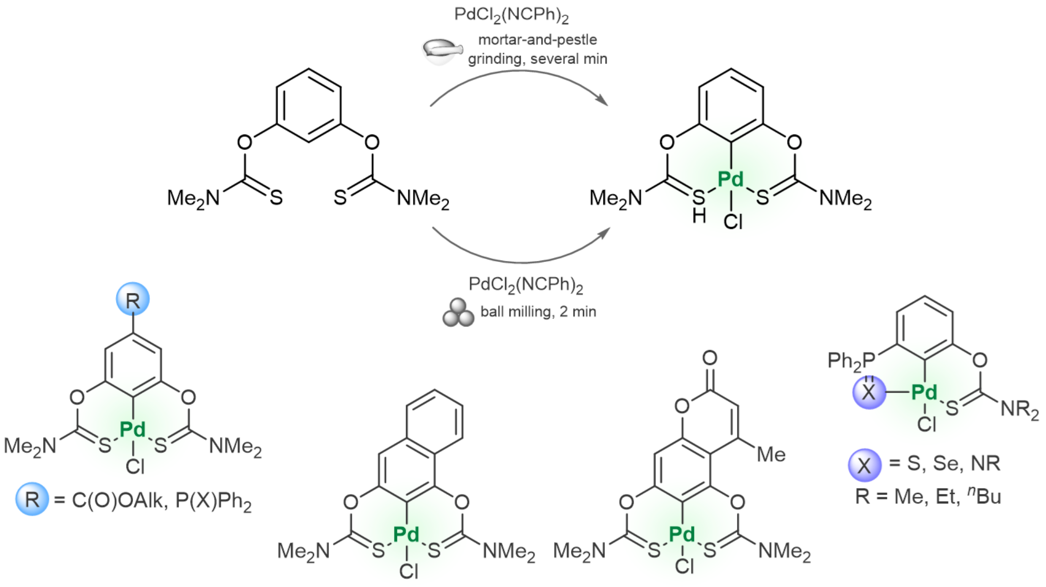
Over the last two decades, different mechanochemical tools have firmly entered into the field of organometallic chemistry. Although the main focus is still on the various mechanochemically promoted catalytic processes, several important classes of organometallic compounds, including transition metal *N*-heterocyclic carbene and sandwich complexes, have been successfully prepared using mechanochemistry. In 2017, our research group described the first example of mechanochemical synthesis of the so-called pincer-type complexes by grinding a symmetrical bis(thiocarbamate) ligand with $PdCl_2(NCPh)_2$ either in a mortar or in a vibration ball mill on a gram scale [1]. The target complex was isolated in 95% yield just in 2 min of milling and a simple workup procedure. Now this solvent-free approach has been successfully extended to a range of new symmetrical and unsymmetrical pincer systems featuring thiocarbamate donor groups, which will be discussed in detail during the report. The results will be supplemented by the insights into the mechanism of mechanochemical C–H bond activation in both *C*- and *N*-metalated pincer systems by different physicochemical methods.



This work was supported by the Russian Science Foundation, project no. 22-13-00267.

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THE PECULIARITIES OF PHASE EQUILIBRIA IN THE Eu-Mn-O SYSTEM WITH MULTIVALENT EUROPIUM IONS

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Phase equilibria in a wide concentration range in the ternary Eu–Mn–O system were studied by pXRD and TG-DSC methods using the mixtures of precursors mechanically preactivated and calcined under an oxygen pressure of 10^{-5}–10^{2} kPa (773-1373 K) and in those annealed under a reductive atmosphere at a partial hydrogen pressure of about 5 kPa (873-1273 K). As a result, the x–y (see fig. below) and p(O_2)–T of the P–T–x–y diagram of the Eu–Mn–O system as well as the selected x–y isotherms of the quasiternary Eu_2O_3 –MnO–MnO_2 system were constructed. For the synthesis of samples a wide range of precursors have been used- Li_2CO_3, $LiOH·H_2O$, LiH, Eu_2O_3, Eu, MnO_2, Mn_2O_3, Mn_3O_4 and MnO.

According to the experimentally observed data, it was eloquently shown, that in stable equilibria the Eu^{2+}-ion containing phases- mixed-valence Eu_3O_4 and europium(II) monoxide EuO coexist exclusively with metallic manganese [1].

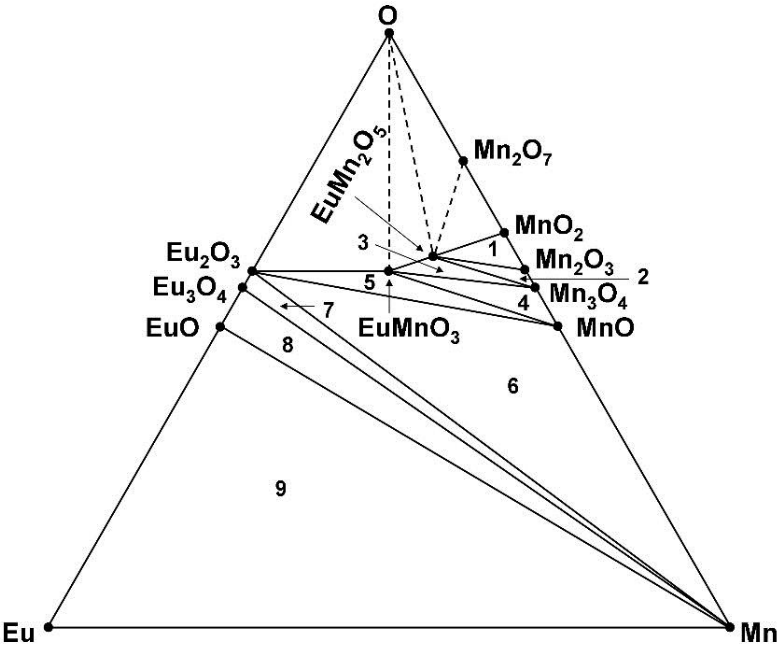

Fig. x-y projection of subsolidus phase equilibria in the Eu-Mn-O system.

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APPLICATION OF EXPLOSIVE LOADING FOR OBTAINING METASTABLE MATERIALS TiFe+Ti$_2$Fe WITH INCREASED HYDROGEN CAPACITY

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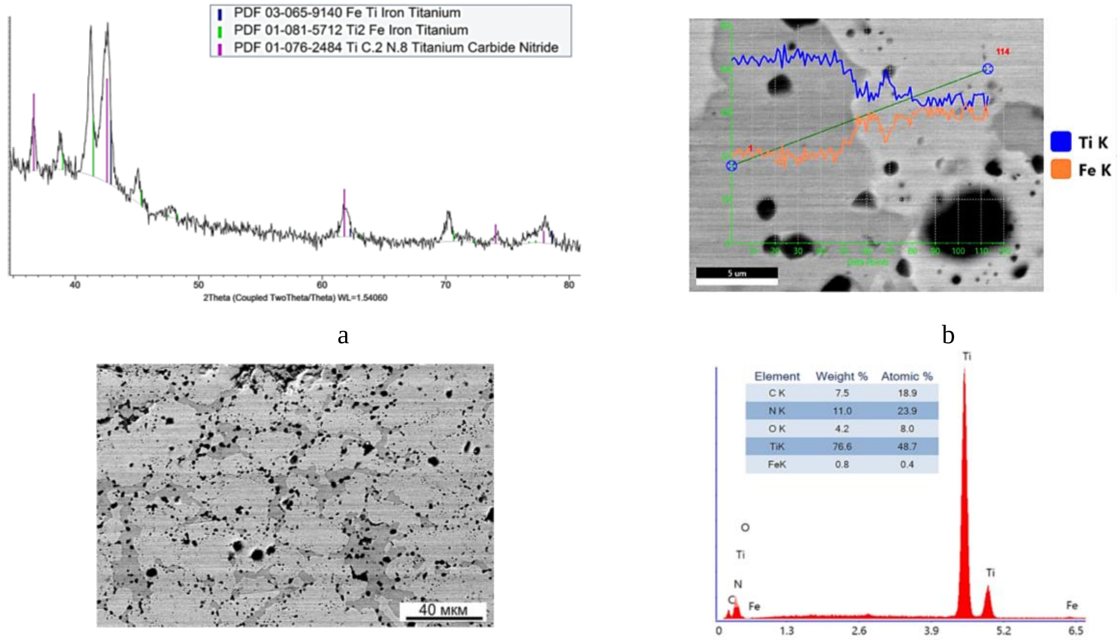
The possibility of obtaining thermodynamically nonequilibrium materials based on TiFe + Ti$_2$Fe (Fig. 1, a, b) using explosive pressing of mixtures of powders of titanium and iron with subsequent reaction sintering of pressed material has been studied. The content of metastable phase Ti$_2$Fe in the material with 57 at.% Ti and 43 at.% Fe was 17.4 vol.% (Fig. 1, c). Thus the accompanying impurities of introduction (oxygen, nitrogen and carbon), rendering negative influence on hydrogen capacity TiFe, have appeared bound in carbonitrides (Fig. 1, d). The increase of titanium content in the initial mixture of powders up to 67 at.% leads to the increase of Ti$_2$Fe content up to 62.1 vol.%.



a

b

Element	Weight %	Atomic %
C K	7.5	18.9
N K	11.0	23.9
O K	4.2	8.0
TiK	76.6	48.7
FeK	0.8	0.4

c

d

Fig. 1. Phase composition (a), microstructure (в, c) and chemical composition of carbonitride inclusions (d) in the powder material containing 57 at.% Ti and 43 at.% Fe after the explosive pressing and reaction sintering.

The hydrogen adsorption properties of the obtained material were determined. It has been established that the total limiting hydrogen absorption by the surface of the material based on the thermodynamically nonequilibrium intermetallide Ti$_2$Fe (67 at.% Ti) appears to be almost three times higher than in hydrogenation of the material based on thermodynamically equilibrium intermetallide TiFe (57 at.% Ti).

MECHANICALLY STIMULATED REDOX REACTIONS IN THE SYNTHESIS OF HIGHLY DISPERSED METALS

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Reactions of reduction of solid metal oxides with active metals (Me_{akt}), which proceed with a large exothermic effect, can be carried out in the process of mechanical activation alone and are mechanically stimulated reactions (MSR). The target products of MSR are Me/(active metal oxide) composites, where Me is the metal of the oxide being reduced. It is advisable to choose the conditions for the synthesis of finely dispersed metals in MSR so that the formed by-products are easily dissolved in traditional chemical solvents, and highly dispersed metal particles would be insoluble in them. As a Me_{act}, the use of magnesium is rational. During mechanical activation of solid mixtures of metal oxides with magnesium, local mechanical melting of Mg particles (T_m = 923 K) occurs with cladding of metal oxide particles and the formation of the MgO phase (T_m ~ 3000 K), which prevents sintering of activation products and when interacting with aqueous solutions of HCl or H_2SO_4 forms highly soluble compounds. The purpose of this work is to study the conditions of mechanically stimulated reduction of GeO_2, Cu_2O, CuO, WO_3, MoO_3, Nb_2O_5, $MgWO_4$, $MgMoO_4$ and $MgNb_2O_6$ by magnesium with the formation of Me/MgO composites and the separation of highly dispersed metals from them during acid dissolution of magnesium oxide and other by-products. X-ray phase analysis showed that Me (Mo, W, Nb)/MgO and Cu(Ge)/MgO composites are formed after 8 and 2(4) minutes of activation of solid mixtures metal oxides with magnesium, respectively, at a drum rotation speed around a common axis of 1000 rpm and the required ratios of metal oxides to magnesium. Highly dispersed metal powders obtained as the result of acid separating MgO from Me/MgO composites were analyzed by energy dispersive analysis for magnesium content (<2%). The particle sizes of samples of the obtained highly dispersed metals were determined from the results of scanning electron microscopy (~100 nm). The conducted studies demonstrate the possibility of obtaining highly dispersed powders of Ge, Cu, W, Mo, Nb by the method of mechanically stimulated redox reactions at room temperature with a high (98%) yield and the possibility of utilizing magnesium oxide by known methods.

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DETONATION SPRAYING OF METAL POWDER MIXTURES

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At present, the structure and properties of medium- and high-entropy alloys are actively studied. Multicomponent Metallic solid solutions with comparable concentrations of the constituents are attractive from both fundamental and applied perspectives. In this work a medium-entropy alloy, FeCoNiCu, was selected as a model system to demonstrate the possibility of fabricating solid solution-type alloy coatings by detonation spraying. A mixture of Fe + Co + Ni + Cu powders was first treated in a high-energy planetary ball mill. The evolution of the microstructure of the FeCoNiCu alloy particles with the milling time was investigated. After 20 min of milling, the powder was nearly a singlephase solid solution of face-centered cubic structure. A bulk alloy was obtained by consolidating the ball-milled powders by spark plasma sintering. The coatings and sintered material were studied by x-ray diffraction and scanning electron microscopy/energy-dispersive spectroscopy/elemental mapping. No oxidation of the material occurred during detonation spraying. The coatings and sintered alloy obtained from the powder mixture milled for 20 min were nearly single-phase with a major phase of face-centered cubic structure. The residual porosity of the coatings and sintered alloy was as low as ~1%. The hardness values of the coatings and sintered alloy were found to be close to each other (~400 HV_{300}). This work showed that a combination of high-energy milling and detonation spraying is a viable route for the formation of nearly single-phase medium-entropy FeCoNiCu alloy coatings.

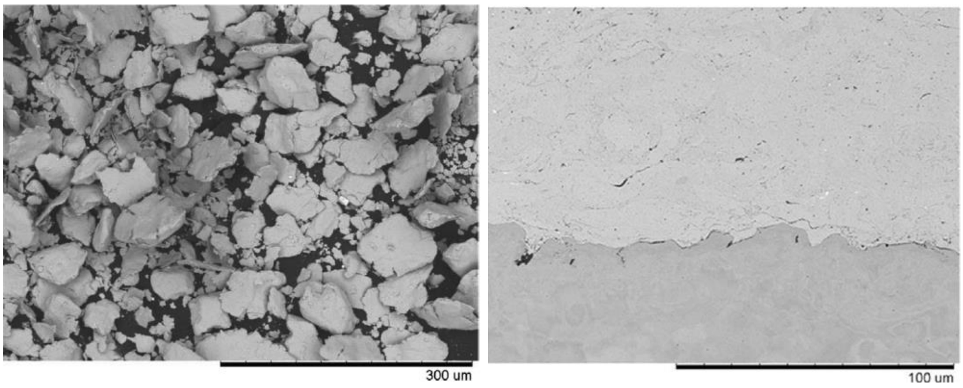

Fig. 1. *a* - Morphology of the FeCoNiCu powder high-energy ball-milled for 20 min;
b - microstructure of detonation coating obtained by ball-milled powder.

THE PHASE STATE OF THE PRODUCTS OBTAINED UNDER CONDITIONS OF SHOCK-WAVE SYNTHESIS OF MECHANOCOMPOSITES OF Ti-Al SYSTEM

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For investigating the processes of self-propagating high-temperature synthesis, methods of rapid heating of the mixture are used. To implement a process in which heterogeneous synthesis is combined with ultrafast heating, the detonation-gas sputtering method was taken as a basis. Although the main task of the detonation-gas sputtering is to obtain protective coatings from powder materials, it is well known that during the detonation-gas sputtering particle velocities reach 300-400 m/s, and gas jet temperatures can reach 2000 °C or more.

Model experiments on shock-wave synthesis of mechanocomposites of 64% Ti (wt.%) +Al composition in the developed pulsed flow reactor have been carried out. A planetary ball mill «Activator-2SL» was used to activate the mixture. Activation times were 3, 5 and 7 minutes. Mechanoactivated precursors with different mechanical activation times were divided into four fractions (<50 microns, 50...100 microns, 100...160 microns and >160 microns) and subjected to extreme thermal effects. It has been experimentally established that different times of mechanical activation and different granulometry of powders do not affect the qualitative phase composition of the reaction products. The composition of the reaction products includes amorphized Al, under-reacted Ti, intermetallic compounds TiAl, $TiAl_3$ and Ti_3Al, as well as nuclei of metastable phases or solid solutions based on Ti, which are in a nonequilibrium weakly ordered state. It was revealed that with varying mechanical activation times and granulometric composition, the quantitative content of the phase composition of the final products changes. The microstructures of the obtained samples confirm the formation of a multiphase product with a partially ordered structure having amorphous and crystalline components.

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TAILORING BORON-MODIFIED AUSTENITIC STAINLESS STEELS FOR ADDITIVE MANUFACTURING: FROM THERMODYNAMIC MODELING TO CORROSION BEHAVIOR

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The mechanical and wear properties 316L stainless steel (316LSS) produced by Laser Powder Bed Fusion (L-PBF) have been extensively evaluated [1]. Wear resistance of steels can be enhanced by boron additions forming Cr,Mo-rich borides, which can be deleterious to corrosion resistance [2]. Incorporating boron to 316LSS powders have not been reported in the literature. This work is a first step to develop B-rich 316LSS powders for L-PBF. Here, the authors aimed to produce 316L steel with boron additions by suction casting and evaluate its corrosion behavior, tailoring the chemical composition to maintain a high corrosion resistance. First, the alloy was modeled through thermodynamic calculations with the aid of ThermoCalc® software. The alloys modeled with 0.50 and 0.75 wt% B were produced by suction casting and submitted to corrosion tests in 0.6 M NaCl solution. The analysis of the samples indicated that there were no losses in corrosion resistance, indicating that the alloy modeling was effective to obtain the presence of borides rich in Mo and Cr dispersed in a matrix with chemical composition equivalent to 316L steel and as corroborated by scanning electron microscopy and X-ray diffraction. In addition, the analysis of the corroded surface indicates that there was preferential nucleation of pits inside the boride network.

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MECHANOCHEMICAL SYNTHESIS OF COMPOSITE INSTRUMENTAL AND TRIBOLOGICAL MATERIALS

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Mechanochemical processing is one of the promising techniques of solids for obtaining new state of substances as a result the conversion of mechanical energy into physical-chemical processes of their structuring. During high-energy mechanical action, solids goes through a number of structural changes and interactions, the general kinetics of which, for example, in metal mixtures, is described by a sigmoidal curve. In accordance with it, the following stages of powder formation are distinguished: finely dispersed composite agglomerates with high reactivity; with a composite structure and grain-boundary phases; the synthesis of a new compound. Examples of the use of mechanocomposites in the application to the creation of materials for instrumental and tribotechnical purposes are considered. In particular, the following powders were obtained: mechanoactivated composites based on boron nitride, ultrahigh molecular weight polyethylene compounds UHMWPE/B4C, UHMWPE/B4C/W; mechanocomposites – Cu/Ti, Cu/Zr, Fe/Ti, Fe/Zr, Fe/diamond, Fe/B4C, B_4C/W; synthesized supersaturated solid solutions are Cu(Sn,Ti), Cu(Sn), Cu(Al,Sn) and composites with a metal matrix Fe/ZrO_2, Fe/TiO_2. Technological schemes of sintering the obtained powders of mechanocomposites, as well as features of the formation of the structure and properties of materials based on them are considered.

The developed compositions have found application as binding materials for the production of diamond-abrasive tools, magnetic-abrasive working media, powders for gas-plasma and centrifugal induction surfacing of parts of friction units and radiation-protective elements.

METALLIC ANTIFRICTION MATERIALS OF Cu-Sn-Al SYSTEM

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Tin bronzes possess antifriction properties, high corrosion resistance and fabricability. However, the fact they have low hardness and strength leads to a necessity to develop modifying and reinforcing additives. Strength characteristics as well as plasticity of the material are determined by wetting of additives and their uniformity of distribution. It is promisingly to use intermetallics having high degree of wetting by matrix material as modifying additives. In this regard modifying tin bronzes by Cu-based intermetallics is of interest.

The influence of mechanical activation of Cu-12 wt.% Sn mixtures with different Cu_9Al_4 modifier contents on physical, mechanical and tribotechnical characteristics of composites obtained by sintering under pressure has been investigated. By using XRD analysis, optical and electron microscopy structural and phase composition as well as morphology of composites formed have also been studied. It has been shown that modification of mechanically activated Cu-12 wt.% Sn bronze by Cu_9Al_4 results in decrease of wear capacity by 1.4-1.8 times and coefficient of friction f by the factor of 2. The stable value of $f = 0.5$ is reached for mechanically activated Cu-12 wt.% Sn + 20 wt.% Cu_9Al_4 composite. Introducing the Cu_9Al_4 intermetallic leads to the increase in microhardness of the composites by 1.6-2 times relating to the BrOF 10-1 bronze and mechanically activated unreinforced bronze.

The work was fulfilled within the framework of state assignment of the ISSCM SB RAS (project No. 121032500062-4), state program of scientific research “Materials science, new materials and technologies” assignment 2.11 of JIME NASB and state assignment of IMET UB RAS (project No. 122020100287-1).

MECHANICALLY ACTIVATED MODIFIERS FOR POLYMERIC MATERIALS

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Composite materials are a mixture of two or more constituent substances with different physical and chemical properties. They have functional characteristics that cannot be achieved with single materials. Mechanochemical methods that induce chemical reactions by applying mechanical energy can significantly increase the affinity between different types of materials. Mechanochemistry methods are carried out in dry conditions without solvents, which makes them relatively simple processes, cost-effective and environmentally friendly. In addition, such methods for the production of composites are well suited for polymeric materials. Since they are compatible with conventional compounding processes and can be used with very fine fillers, including nanomaterials. Recently developed mechanochemical processes in combination with plasma treatment can form a covalent bond between chemically less active materials, even in the solid state. This compounding method is called plasma-assisted mechanochemistry. Compounding by mechanochemistry can be an effective solution to a fundamental problem in the formation of polymer nanocomposites, i.e. poor compatibility of polymers and nanofillers.

The structure of polymeric materials and compositions based on them significantly depends on the technological regimes under which the deformation of these systems is carried out. The use of mechanical activation leads to a significant structural change in polymeric materials and their compositions observed in a state of local thermodynamic equilibrium. The kinetics of the mechanical activation processes, which is determined by the parameters ko, E, are entropy and energy characteristics. A relationship has been established between the degree of crystallinity of polymeric mechanically activated systems and the time of mechanical activation under the same conditions for processing composite materials. The main physical and mechanical characteristics of composite materials on a polymer matrix, obtained by modification with low-dimensional mechanically activated nanoparticles, are determined. It has been shown that the introduction of mechanically activated particles into thermoplastic polymer matrices increases the Shore and Brinell hardness values by 18–27%, depending on the concentration of the modifier.

MECHANOCHEMICAL SYNTHESIS OF THE HAFNIUM NITRIDE AND CARBONITRIDE POWDERS BY THE DIRECT NITRIDATION OF Hf AND (Hf+C) PARTICLES IN A PLANETARY MILL

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Refractory ceramics materials to date are one of the most future-oriented compounds for different applications, especially in aerospace industry. This class of materials can work under extreme conditions, withstand high temperatures, mechanical stress, as well as radiation and wear. Particular attention is paid to carbides, nitrides and carbonitrides of transition metals, which poses high chemical and mechanical properties. A promising route for obtaining such materials in powder form is mechanochemical synthesis (MS), since it does not require high temperatures and allow obtaining materials with the required composition in a relatively short period. The possibilities of synthesis are greatly expanded by the use of the reaction gas during MS. Since no external preheating of the reaction volume is required, such mechanically induced solid-gas reactions have attracted much attention. Thus, the aim of this work was to synthesize refractory hafnium nitride and hafnium carbonitride powders by the MS route through direct nitridation of Hf and (Hf+C) particles in nitrogen atmosphere during high-energy milling in a planetary ball mill. The phase composition and the evolution of the microstructure of the powders were studied. Obtained Hf(C,N) powders were also consolidated by spark plasma sintering, the structure and properties of the fabricated bulk ceramics were also investigated.

This study was conducted with financial support from the Russian Science Foundation Grant No. 19-79-10280-П.

STUDY OF THE POSSIBILITY OF OBTAINING COMPOSITES Al/MLCN USING MECHANICAL PROCESSING AND ELECTRON BEAMS

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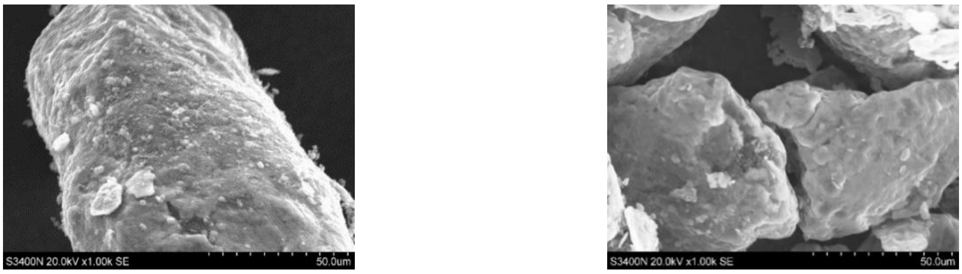
In this work, the impact of the joint mechanical processing (MP) of aluminum powders and multi-layer carbon nanotubes (MLCN) on the properties of Al/MLCN composites obtained by electron-beam swimming vanity was conducted.

The Budker Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences (BINP SB RAS) has developed a unique technical equipment for performing electron-beam welding or metal floating in a vacuum.

It was determined that, as a result of mechanical treatment for 5 min, MLCNs were distributed over the surface of aluminum particles (Fig. 1a). The presence of MLCN coating on the particles surface did not allow the powder to stick together during MP, but the same was observed as a result of fusion with a bundle. The introduction of 2 wt.% copper into the powder mixture, followed by joint MP, will lead to an increase in the plasticity of the composition and the absence of characteristic MLCN threads on the surface of aluminum particles (Fig. 1b).



a) Al + 2 % MLCN M2 b) Al + 2% Cu + 2 % MLCN M2

Fig. 1. Microphotography of master blows based on aluminum powder, copper and MLCN.

This work was conducted within the framework of the budget project No. 12103250071-6 of the Institute of Solid State Chemistry and Mechanochemistry SB RAS and the target Program in accordance with Agreement No. 075-15-2021-1359 dated 13.10.2021 (Internal number 15.SIN.21.0015).

MECHANOCHEMISTRY OF PLANT MATERIALS: OVERVIEW OF THE KEY EFFECTS

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Plant material is a complex multicomponent system. In its most general form, it can be divided into a polymer composite matrix and low molecular weight substances distributed in the matrix in a certain way. Mechanical treatment of such a system in a mixture with reagents leads to a cascade of processes. When processing of medium intensity (for example, in a planetary mill with an acceleration of grinding bodies of 20 g), one can find the sequence of the processes.

At the first stage, the raw material is grinded, usually to a particle size of 200-300 micrometers. With further grinding (a few minutes), in addition to size reduction, plastic deformation of the matrix - amorphization of the structure occurs. Plastic deformation is a necessary condition for ensuring mass transfer in solid particles and the occurrence of chemical reactions of low molecular weight substances. The disordering of the matrix structure at the first stages greatly facilitates diffusion and accelerates the processes during the extraction of minor components with solvents. Subsequently, “particle compaction” occurs, the destruction of pores - effective diffusion channels - leading to a drop in the diffusion characteristics of low molecular weight substances. In this case, the chemical composition of the matrix changes only slightly. A mathematical model is presented that takes into account the considered processes. Processing products can be used to improve the efficiency of isolation of low molecular weight components.

Long-term treatment for tens of minutes mainly leads to the destruction of low molecular weight substances. In this case, the chemical composition of the matrix also changes - depolymerization of lignin and cellulose proceeds. Examples of the use of products of long-term mechanical processing in the production of sorbents, biofuels, and solid powder fuels are given.

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WAYS OF MECHANICAL ENERGY RELAXATION IN CELLULOSE

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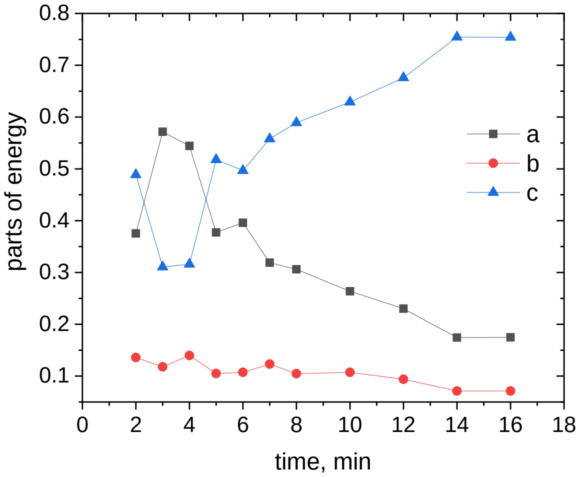
Mechanical treatment can serve for different tasks: size reduction, destroying of complex material microstructure or specifical impact at level of individual molecule. Often all these processes occur simultaneously, but ratio between them can be different. So, if we want to optimize technology for mechanical treatment of plant raw materials, we must to understand which part of applied energy goes at desired channel. Construction of such description can be very difficult and then it is unpopular research.

Here we propose a simple approach to estimation of mechanical energy expenditure ways at processing of alpha-cellulose [1]. Our approach based on two main assumptions: 1) part of the total applied energy spent on the material destruction does not change during the experiment 2) destruction goes at three ways: size reduction (**a**), amorphization of crystal structure (**b**) and depolymerization (**c**).

We found that the main processes are size reduction and depolymerization, and they have an opposite tendency: size reductions part decreased in time, but depolymerization part increased. Our results important for development of mechanochemical technology and estimation of its economical effectivity.



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DETERMINATION OF THE CRYSTALLINITY INDEX OF CHITOSAN WITH DIFFERENT MOLECULAR WEIGHTS DURING MECHANICAL TREATMENT

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Mechanical amorphization of three chitosan samples (high, medium, and low molecular weight) was studied. Different techniques for determining the crystallinity index (CrI) of polymers (analysis of the X-ray diffraction data, the peak height method, the amorphous standard method, peak deconvolution, and full-profile Rietveld analysis) were compared. The peak height method has a wider operating range, but gives deviated CrI values for the samples consisting of a mixture of polymorphic modifications. Taking into account the multiple inconsistencies in the suggested structure file of chitosan, it is not recommended that neither it nor periodic DFT optimized structures are used for Rietveld analysis. Long-term mechanical treatment of chitosan with different molecular weights in a planetary ball mill provides characteristic amorphous XRD profiles, so the resulting amorphous samples can be used as standards for determining the crystallinity index. The proposed equation describing the profile of the averaged amorphous sample can be used to determine the crystallinity index (using the amorphous standard method and by deconvolution of XRD patterns) for arbitrary chitosan samples. Power consumption for mechanical amorphization of chitosan did not differ significantly for the analyzed samples with different molecular weights and was 28 kJ/g, which is comparable with the energy input for cellulose amorphization determined earlier (29 kJ/g), and 5-7 times higher than for amorphization of polymorphic starch modifications (4-6 kJ/g) [1].

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STUDY OF THE EFFECT OF ENCAPSULATION ON THE KINETICS OF OXIDATION OF GREEN TEA CATECHINS BY ATMOSPHERIC OXYGEN

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The biological benefits of green tea are due to its content of flavonols, which make up 6-16% of dried green tea leaves in mass. Tea flavonols are a group of naturally occurring polyphenols found in green and black teas. Green tea contains four flavonol derivatives: epicatechin (EC), epigallocatechin (EGC), EC gallate (ECG), and EGC gallate (EGCG). Their biological benefit stems from their strong antioxidant and anti-angiogenic activity, as well as their ability to inhibit cell proliferation and modulate carcinogen metabolism.

The problems of storage and delivery of catechins to the cells of the body lie in their instability upon contact with atmospheric oxygen (especially with increase in temperature), dependence on the pH of the medium in dissolved form, and degradation during digestion.

To a certain extent, this problem is solved by using the microencapsulation method, which involves physical incorporation of sensitive biologically active compounds into the matrix of macromolecules, which leads to an increase in resistance of catechins to environmental conditions.

The purpose of this work is to obtain and characterize dry extract of green tea and encapsulate of green tea (maltodextrin was used as encapsulating material). This study developed and elaborated methods for obtaining and oxidizing samples of green tea extract and green tea encapsulate. The resulting samples were characterized by HPLC and SEM. The degree of catechin encapsulation was determined to be 92.1% for EGC, 94.8% for EGCG, and 100% for ECG. A procedure was also developed for oxidizing samples by atmospheric oxygen at various temperatures (65-70 °C for the extract and 144 °C for the encapsulate). Constants of effective rates of oxidation of samples (K_{eff}) were calculated in pseudo-first order approximation, as well as the activation energy of the oxidation reaction of green tea extract with atmospheric oxygen (E_a). It was found that the effective oxidation rate constants of the extract at 70 °C are rather close in value to the effective oxidation rate constants of the encapsulate at 144 °C, which indicates an increase in resistance of catechins to oxidation by atmospheric oxygen as a result of encapsulation.

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RADIATION-THERMAL SYNTHESIS OF COPOLYMERS OF CHITOSAN WITH ACRYLAMIDE AND STUDY OF THEIR PROPERTIES

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In recent years, chitosan and its derivatives have attracted increasing interest due to the unique properties of chitosan associated with its environmental friendliness, high biological activity, reactivity, biocompatibility and biodegradability [1,2].

Obtaining copolymers of various structure and composition, in turn, opens up the possibility of creating "smart" materials that can change properties when exposed to temperature, light, pH, and other external factors.

The aim of this work was to obtain composites with controlled release of betulin into solution. For these purposes, graft copolymers of chitosan with acrylamide were obtained using ionizing radiation with treatment doses 6-160 kGy. The formation of graft copolymers was confirmed by IR and NMR spectroscopy and gel permeation chromatography. A high yield of the product and its solubility are observed at radiation doses of 12-40 kGy. With a further increase in the dose, a decrease in the solubility and yield of the product is observed. The study of the molecular weight distribution showed that a significant amount of the original chitosan remains in the samples.

Mechanochemical activation of the copolymer leads to an increase in solubility for samples obtained at doses of 80 and 160 kGy. The gel-penetrating chromatography method showed different sensitivity of the components to mechanochemical activation - the initial low molecular weight chitosan does not undergo cracking.

With joint mechanochemical activation, composites with betulin were obtained. The rate of release of betulin into an aqueous solution during the dissolution of the mechanocomposite depends on the pH of the solution, which makes it possible to consider the obtained composites as promising means for the controlled delivery of betulin, as well as other biologically active substances.

This work was supported by the Ministry of Education and Science of the Russian Federation (project No. 122032900067-4).

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PREPARATIONS BASED ON FENBENDAZOLE OBTAINED BY METHODS OF MECHANOCHEMISTRY, THEIR STABILITY AND EFFICACY

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To combat helminthiases in cattle, the most widely used drug is fenbendazole (FBZ), which has a wide spectrum of anthelmintic action. However, FBZ is poorly soluble in water and has low absorption in the digestive tract, which in turn is the cause of poor bioavailability and therefore part of the drug is excreted from the body without being absorbed.

To increase the solubility of the FBZ substance, we used mechanochemistry methods, which made it possible to obtain:

- solid dispersions (SD), consisting of two components (FBZ, polymer) /I/;
- SD of three components (FBZ, succinic acid, polymer) /II/;
- products of the interaction of FBZ with succinic acid in organic solvents /III/.

By using HPLC/MS and NMR, it has been shown that:

- upon receipt of SD by methods I and II, FBZ destruction does not occur either during mechanical processing or during their storage for up to 7 years.
- when combining the methods of mechanochemistry and the interaction of FBZ with succinic acid in the various solvents, destruction of FBZ to its oxide (up to 23%) is observed.

The study of the nematodocidal activity of the obtained preparations of fenbendazole showed that in experimental trichinosis:

- the most active forms of FBZ use are its SD with PVP and with AG;
- SD based on FBZ with succinic acid turned out to be inactive, contrary to our expectations that more soluble salt forms from FBZ (weak base) and succinic acid (strong acid) should have been formed during the joint mechanical treatment.
- products according to the method III showed weak activity, because they consisted of FBZ (75–96%), which did not allow reaching a therapeutic dose.

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OBTAINING PHARMACEUTICAL CO-AMORPHOUS SYSTEMS OF AN ANTHELMINTIC DRUG FLUBENDAZOLE USING MECHANOACTIVATION METHOD

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One of the urgent problems in the creation of new active pharmaceutical ingredients (API) is their low solubility in water [1,2]. As a result, the drug has low rates of efficacy and bioavailability. Therefore, at present, the amorphization method is widely used in pharmaceuticals as an effective way to increase the solubility of APIs [3]. However, amorphous forms of APIs have low physical stability. This problem can be solved by co-amorphization with a low molecular weight compound, such as amino acids. In our work, amorphous and co-amorphous forms of the widely used in clinical practice anthelmintic drug flubendazole (FluBZ) were obtained and studied. As the second components, amino acids safe for the body were chosen. As a result of mechanochemical screening, two new co-amorphous forms with L-phenylalanine (Phe) and L-tryptophan (Trp) were found in 1:1 stoichiometry: FluBZ-Phe (1:1) and FluBZ-Trp (1:1). For these systems, the optimal conditions for obtaining the best yield were selected. New systems were analyzed using differential scanning calorimetry (DSC), X-ray phase analysis (XRD), infrared spectroscopy (IR) and scanning electron microscopy (SEM), as well as experiments on physical stability at various humidity and study of dissolution processes in biorelevant media simulating environment of the gastrointestinal tract.

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ALKYL DERIVATIVES OF CHITOSAN AS FILLERS IN POLYOLEFINE FILMS

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Polyethylene and polypropylene are actively used as a packaging material due to their mechanical properties and low cost. However, the wide application of these polymers for packaging industry results in environmental pollution due to its low biodegradation rate. Filling polyolefines with biodegradable natural polymers, such as chitosan, could bring antimicrobial activity and biodegradability to such composite materials. However, chitosan is thermodynamically poorly compatible with polyolefines. Hydrophobic modification of chitosan could be used to increase its affinity for synthetic polymers. Such combination is the promising way to obtain materials with acceptable physical-chemical and mechanical properties and a shorter degradation time compared to non-modified synthetic polymers, which in turn can be an important alternative to reduce plastic waste pollution.

The aim of this work was the mechanochemically induced derivatization of chitosan and study of the properties of the composite films made of polyolefines and alkyl derivatives of chitosan. The derivatives were obtained by mechanochemical modification of chitosan of various molecular weights with docosyl- and hexadecylglycidyl ethers using a twin-screw extruder. Mixtures of polyolefines with the obtained alkyl derivatives at various ratios (10, 20, 40, and 70 wt.%) were obtained by both solid-state extrusion and in a melt using a closed type mixer (Brabender). The composite film materials were cast using compression molding, followed by a study of their physical-chemical and mechanical properties, including moisture absorption and morphology. The properties of the composites were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The data of DSC and TGA showed that the melting point of the mixtures decreased slightly with an increase in the concentration of alkylated derivatives and an increase in the crystallinity of the mixtures occurred. A tensile study showed that an increase in the proportion of chitosan derivatives in film samples reduces their mechanical characteristics of the PE-based patterns. In the case of polypropylene, the decrease in mechanical strength is not so pronounced and is accompanied by an increase in the plasticity of film samples. The addition of alkylated derivatives to polyolefins also led to an increase in water absorption by films.

STUDY OF SELF-ASSOCIATES OF ARABINOGALACTAN, GLYCYRRHISIC ACID, AND POLYVINYLPIRROLIDONE MACROMOLECULES WITH SALICYLIC ACID IN AQUEOUS SOLUTIONS BY THE DYNAMIC LIGHT SCATTERING METHOD

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Arabinogalactans (AGs) are a class of polysaccharides found in a wide variety of plants. The branched structure of AG made it possible to use AG as a host molecule for drugs and to create inclusion complexes based on it [1]. Glycyrrhizic acid (GA) - licorice root extract, in the drug delivery system has a strong complexing ability for drugs and self-association in an aqueous solution. Emphasis is placed on natural polysaccharides due to their good biocompatibility, good stability, safety and adhesive properties. Polyvinylpyrrolidone (PVP) is a safe, water-soluble polymer with various molecular weights and viscosities. A large number of reports have claimed that the use of PVP can increase the dissolution rate and bioavailability of drugs and combine stabilization through hydrogen bond interaction [2]. Salicylic acid is of interest as a medicinal substance with a pronounced anti-inflammatory effect, it is poorly soluble in water (1.8 g/l at +20 °C).

The purpose of our work is to study the molecular mechanisms of the formation of supramolecular systems in aqueous solutions obtained from solid dispersions of combinations of the above substances. The inclusion of drug molecules in such complexes makes it possible to increase water solubility and bioavailability and to significantly reduce effective dosages and toxic effects [3].

Suitable parameters for the preparation of solid dispersions have been investigated. The characteristics of AG, GA, and PVP solutions were studied at various temperatures and concentrations by dynamic light scattering (DLS). In all cases, a significant degree of self-association is shown in units of change in their molecular weights (kDa) and the dependence of these characteristics on the specified conditions.

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DESIGN AND SYNTHESIS OF CARBAMAZEPINE TERNARY COCRYSTALS

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Ternary cocrystals have recently gained attention from researches for drugs to improve its physicochemical properties such as solubility, dissolution rate, permeability and others. At the same time, its preparation is quite challenging task. The primary challenge is the great variety of different phases which can be obtained in the process of liquid-assisted grinding and solution crystallization (initial components, binary cocrystals, solvates, polymorphs, ect.). Design of ternary cocrystal is based on several approaches [1], but its formation is still unpredictable and structures of the resulting crystals are often random.

The aim of this study is to investigate carbamazepine ternary cocrystal formation processes. Carbamazepine is known as an anticonvulsant and a mood-stabilizing drug used primarily to treat epilepsy, bipolar disorder and trigeminal neuralgia. According to the biopharmaceutical classification system, carbamazepine is classified as a class II drug having low water solubility. More than 40 binary carbamazepine cocrystals are known in literature so we supposed that propensity of ternary cocrystal formation for this compound is also very high.

In the present work, «drug-bridge-drug» strategy was utilized for suitable coformers selection [2]. Experimental screening has been performed for 32 ternary carbamazepine systems via liquid-assisted grinding with acetonitrile addition as a solvent. As a result, two isostructural ternary cocrystals have been obtained and characterized using powder X-ray diffraction method and differential scanning calorimetry. Besides, five new binary phases have been identified in cocrystal preparation process. Single crystals of ternary forms have been grown by slow evaporation method and its crystal structures have been resolved using single crystal X-ray diffraction. Relative stability of binary and ternary cocrystals was evaluated by competitive grinding.

The research is supported by grant of the Russian Science Foundation № 22-13-00031.

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EFFECT OF MECHANOCHEMICAL ACTIVATION ON THE PHARMACEUTICAL SUBSTANCE LEVOFLOXACIN PROPERTIES

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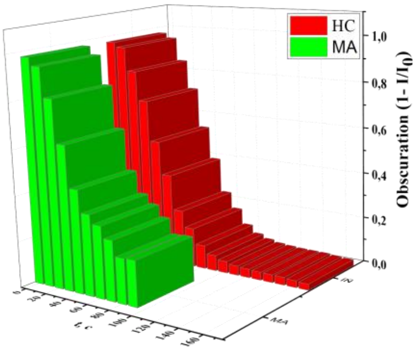
Mechanochemistry, according to experts, contributes to the development of unconventional "chemical thinking", open up new horizons on the path of "green chemistry" and the study of new properties of already known materials [1]. When applied to the chemistry of pharmaceuticals, this provides an opportunity to study their repositioning - a change in brand status through the identification of new physico-chemical properties and biological activity [2]. The main parameters of mechanoactivation (MA) are the pressure and shear, strain rate and temperature of the sample, which promote the formation of centers with increased activity on the newly formed substance surfaces and, as a result, the modification of properties without a long process of new synthesis [3].

The object of study in this work is a sparingly soluble in water levofloxacin (Lvf) substance powder from the fluoroquinolone group. It was microstructured in a free, direct-impact (Rumpf) pulsed mode in a grinding knife mill. The dissolution rate of Lvf native state (NS) and the state after MA in purified water in the was investigated using a low angle laser light scattering (LALLS) technique.



The figure shows an exponential decrease in time the values of the laser obscuration dependent variable, however, with longer duration in the case of NS (red), but higher speed in the case of MA (green). The dissolution rate ($\overline{k}\cdot 10^2$, c^{-1}) was estimated by the coefficient b of the straight line equation $y=a+bx$: $k=0.0300\pm0.002\text{s}^{-1}$ (MA) и $k=0.0245\pm0.004\text{s}^{-1}$ (NS), which corresponds to a dissolution rate increase of 1,2 times: $\frac{k_{\mathrm{MA}}}{k_{NS}} = 1.2$. The modified properties of Lvf after MA allow its solubilisation and hence its pharmacokinetic characteristics to be influenced.

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SYNTHESIS OF POLYLACTIC ACID-E-POLYLYSINE COPOLYMER BY PULSED MECHANOCHEMICAL ACTIONS

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Drug delivery systems based on polymeric materials play a significant role in improving the pharmacological and therapeutic properties of drugs by controlling their pharmacokinetics, biodistribution, and toxicity. Among the wide range of biocompatible and biodegradable polymers used to develop drug delivery systems, biopolyesters and polyamic acids are promising candidates for encapsulating hydrophobic drugs. The paper presents the synthesis of a polylactic acid-ε-polylysine graft copolymer using pulsed mechanochemical effects implemented under the conditions: type 1 - rheological explosion and type 2 - reaction mixing in a vibrating mill, with varying the initial ratio of homopolymers. The structure and properties of the resulting copolymer were characterized by IR spectroscopy, 1H NMR, and dynamic light scattering. The yields of the copolymer were estimated depending on the type of treatment. The effect of a filler in the form of elemental boron nanoparticles, in the size range of 5–15 nm [1, 2], on the properties and yield of a polylactic acid-ε-polylysine copolymer was studied.

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MECHANOCHEMICAL ACTIVATION OF METAL-BEARING BROWN COAL: OXIDATION OF ORGANIC MATTER AND REDISTRIBUTION OF RARE EARTH ELEMENTS

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Mechanochemical activation of brown coals (BC) has shown promise for various tasks. In most applied works, whether to produce sorbents of pollutants or soil ameliorants, mechanochemical transformations of coal are considered in the context of changes in the physicochemical properties and operational characteristics of coal in general; rarely are changes occurring to humic acids (HA) in the composition of coal analyzed [1]. In addition to HA, BCs may contain other valuable substances, such as rare-earth elements. In recent decades, the prospects of some BCs and their ashes for the extraction of rare-earth elements (REE) are stated more and more often.

The report will present the results of the study of the processes occurring during mechanochemical treatment of BC as an ensemble consisting of the organic matter of coal and the mineral component. Special attention is paid to the differences between the mechanochemical oxidation of HA in the composition of lignite and previously isolated HA. The mechanochemical treatment of BC was carried out in a wide range of conditions: from varying the additives of oxidizing and complexing reagents to varying the "technical" characteristics of the treatment, such as the ratio of the mass of grinding bodies to the mass of the coal, the energy loading of the processed mixture during the treatment, etc. The influence of "technical" parameters on the result of oxidation reactions of the organic matter of coal, on the content of paramagnetic centers in coal, and on the tendency of the product particles to form agglomerates is shown. Special attention is given to the task of analyzing the distribution of REE contained in BC between the organic and mineral components and searching for a method of mechanochemical influence on this distribution. The possibility of mechanochemical concentrating of up to 98% of REE contained in coal in HA fraction is shown.

This study was supported by the Russian Science Foundation (project no. 22-73-00192).

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MECHANO-ENZYMATIC ACCELERATION OF STARCH NANOPARTICLE PRODUCTION

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Nanoscale starch particles are widely used in various applications, such as the strengthening of biodegradable films, paint fillers, in the food industry, as drug carriers, adjuvants and many others [1]. However, processes for producing starch particles take 2-6 days, have a low yield and still have the problem of producing nanoparticles on an industrial scale [2]. We propose a method for accelerating the production of starch nanoparticles based on a combination of mechanical, mechanochemical and mechanical-enzymatic processing, which under laboratory conditions results in an essential reduction in the time for the production of starch nanoparticles.

At the first stage, a special treatment of starch is carried out, after which it is possible to make a brittle damage of starch granules at room temperature in the free impact mode in jet mills. It is important to note that in such treatment, the damaged starch granules retain the crystal structure characteristic of native starches. Then the obtained powder undergoes hydro-mechanical treatment in mechanical-enzymatic and mechanochemical reactors. In these reactors, intensive mechanical action is carried out in a hydro-pulse mode as a result of periodic interruption of slurry flows. The sequence of mechano-enzymatic and mechanochemical treatment allows to significantly reduce the time for obtaining starch nanoparticles. This technology allows you to obtain from several tens to several hundred kilograms of the target product per day, depending on the particle size of the nano starch and the duration of the work shift.

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MECHANO-ENZYMATIC TECHNOLOGY OF STARCH BIOCONVERSION

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Biotechnological processing of natural biopolymers in mechanical-enzymatic reactors leads to a wide range of highly profitable import-substituting products. The ongoing processes are multi-stage and difficult to control with changing rheology of the reaction mixture, with changing grain size and chemical composition of the materials being treated. To increase the efficiency of processing starch-containing raw materials, it is proposed to carry out all technological processes in one apparatus - a mechanical-enzymatic reactor of original design. Enzymatic hydrolysis of starches takes place in three successive steps: 1) gelatinization-gelatinization; 2) liquefaction-dextrinization; 3) saccharification. On an industrial scale, stages 1 and 2 are carried out at temperatures of 140-145 0S, and the saccharification step is carried out at 60-650S in another fermenter. The total duration of the starch-to-glucose conversion process is 70-100 hours [1]. In the mechanical-enzymatic reactor of stages 1 and 2, it is carried out at temperatures of 80-85 0S, and the saccharification stage at 60-65 0S. The total duration of the process is 8-10 hours [2]. One explanation for the acceleration of starch hydrolysis in the production of glucose solutions is the intensification of diffusion phenomena, which is carried out by affecting starch substrates with alternating mechanical vibrations over a wide range of frequencies that arise as a result of interruption of liquid flow. This leads to the appearance of shock waves, high shear stresses, cavitation and other physicochemical phenomena, the combination of which ensures the acceleration of enzymatic hydrolysis of starches.

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HYDRODYNAMIC CAVITATION AS A METHOD FOR INTENSIFYING THE PROCESSES OF LIQUID-PHASE OXIDATION OF ORGANIC AND INORGANIC TOXIC SUBSTANCES

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The development of hybrid technologies that combine the processes of liquid-phase catalytic oxidation and cavitation action is one of the promising ways to intensify the processes of degradation of toxic organic and inorganic substances. Under cavitation conditions, the mechanochemical effect on the components of the reaction solution can promote both the intensification of interfacial mass transfer processes and an increase in the rate of formation of highly reactive Red-Ox radicals.

In this work, we demonstrate the results on the kinetics and mechanism of the oxidation of highly alkaline sulfide solutions with oxygen in the presence of a cobalt tetrasulfophthalocyanine catalyst and on the kinetics of the oxidation of chromic dark blue azo dye (ChDB) with oxygen, hydrogen peroxide, and Fenton reagents under conditions of high mass transfer and hydrodynamic cavitation. Oxidation of 0.05-0.15 M Na_2S solution was carried out at 25–40 °C and solution pH = 12.5, 5-10 μmol/L $CoPc(SO_3Na)_4$. Oxidation of 0.08 mM ChDB solution was studied at 25-40 °C and solution pH = 3, H_2O_2/ChDB = 50-150, H_2O_2/Fe^{2+} = 280. Reactions were studied in 2 types of batch reactors: a shaken reactor in which mixing gas and liquid (foaming mode) and a reactor with a rotary generator of hydrodynamic cavitation (foaming mode + cavitation effect).

It was found that the cavitation effect leads to an increase in the rate of Na_2S oxidation in a strongly alkaline medium. It has been established that the mechanochemical activation of the components of the reaction solution under hydrodynamic cavitation conditions accelerates the formation of active intermediates – Sn^{2-} ions. When the catalyst concentration is higher than the critical one (7 μM), the rate of formation of polysulfides exceeds the rate of their destruction, and the slow mechanism of direct oxidation is replaced by a high-speed polysulfide mechanism.

It is shown that the combination of hydrodynamic cavitation with the process of oxidation with Fenton's reagent leads to a 30-fold increase in the rate of the dye oxidation reaction and a 3-fold decrease in the time to reach 100% dye conversion (25 °C, the molar ratio of H_2O_2/ChDB and H_2O_2/Fe^{2+} is equal to 100 and 280, respectively).

TRANSFORMATION OF GLYCEROL IN THE REACTION CYCLOKONDENSATION WITH ACETONE UNDER CONDITIONS OF HYDRODYNAMIC CAVITATION

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The effective way to use glycerin, which in the modern world has an oversupply, is its condensation with aldehin ydes and ketones. In the reaction of glycerol with acetone (Fig. 1), the basic product is 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane (zolketal), which can be used as promising additive to motor fuels that improves their properties.

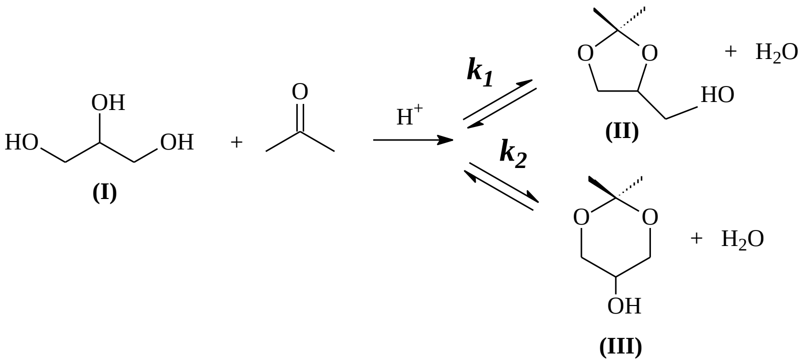

Fig. 1. The cyclocondensation reaction of glycerol (I) with acetone. (II) - zolketal, (III) – ketal- 2,2-dimethyl-1,3-dioxan-5-ol.

The cavitation effect on the reaction system increases exchange mass and chemical processes, contributing to the homogenization of the reaction mixture, reducing diffusion restrictions in the glycerol-acetone-catalyst system. Due to the increase in the turbulence of the liquid flow, the contact interaction between the reactants and the catalyst is activated in the entire volume of the liquid.

In the present work obtained data on the kinetics of the zolketal synthesis reaction from glycerol and acetone in the presence of the zeolite with faujasite structure, in the decationized form, as the catalyst. The reaction was studied at 25 °C, acetone/glycerol molar ratio 2.5, catalyst content 1.6 wt. % with using reactors in batch of the two types: in the stirred reactor and in the reactor with a rotary generator of hydrodynamic cavitation.

It is shown that the cavitation effect leads to increase in the rate of glycerol conversion without changing the selectivity for zolketal.

PREPARATION OF BLACK PHOSPHORUS NANOMATERIALS THROUGH SHOCK-INDUCED PHASE TRANSFORMATION

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2D materials, such as graphene, MoS_2 and transition metal dichalcogenides, have attracted great attention owing to their multiple excellent properties, including mechanical, thermal, optical and electrical properties. Black phosphorus (BP) is a layered semi-conductive allotrope of phosphorus with an intrinsic bandgap, which can be exfoliated to be monolayer and few-layer BP nanosheets or quantum dots triggering further interest in this new elemental 2D-QDs material.

In this study, we investigated the effects of pressure, temperature and precursor morphology on the products. Among them, red phosphorus powder is filled in a sample container and subjected to high shock pressure and temperature using a shock-driven flyer. Well-crystallized black phosphorus nanosheets (a lateral size of 0.5-20 mm and a thickness of 1.5-50 nm) are obtained. Furthermore, the ball-milled red phosphorus powder was shocked to induce phase transformation at transient high pressure and temperature. The characterization results demonstrate that the majority of recovered sample is BP QDs with a lateral size of 2-10 nm and a thickness of 0.9-2 nm. The increase of shock pressure thickens the formed black phosphorus nanosheets and decreases their lateral size. This study also confirms that the micromorphology of precursor is critical to the formation of BP QDs. In addition, the formation mechanism of black phosphorus nanosheets and BP QDs by shock-induced phase transformation of red phosphorus is carefully analyzed.

EFFECT OF MECHANICAL ACTIVATION ON BINDING PROPERTIES OF FLY ASH BLENDED WITH CALCIUM CARBONATE AND GYPSUM

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The possibility of the existence of three-component binder based on the mechanically activated "fly ash - calcite - gypsum dihydrate" mixture and prepared with water was studied. Fly ash from the Apatity Thermal Power Station, calcite concentrate (Kovdor deposit of Murmansk region) and gypsum stone (Arkhangelsk region) were used as raw materials. Mechanical activation (MA) was carried out in a laboratory centrifugal planetary mill AGO-2. The dependence of the compressive strength of this binder on the ratio of source components in the mixture, the duration of their joint MA and curing conditions was investigated.

The compositions containing 1-7 wt.% gypsum, 5-20 wt.% calcite and 73-94 wt.% fly ash after MA for 180-270 s, mixing with water and curing in wet conditions exhibit weak hydraulic properties, however the compressive strength is low, about 1-2 MPa. Apparently, MA- fly ash is the active component in these compositions. The formation of active lime as a result of $CaCO_3$ decomposition due to MA is not also excluded. Small additions of gypsum do not have a noticeable effect on the binding properties of the MA-composition.

The compositions with the increased content of gypsum 20-30%, calcite 10 wt.% and fly ash 60-70 wt.% after MA for 270 s curing in air-dry conditions demonstrate compressive strength up to 9-10 MPa. The increase in the MA time from 180 to 270 s leads to an increase in compressive strength of the composition "fly ash (70%)-$CaCO_3$ (10%)-gypsum (20%)" by more than 2 times. Apparently, this is due to an increase in the degree of gypsum dehydration, which ultimately provides hardening of the gypsum composition [1].

Thus, the MA-mixture "fly ash - calcite - gypsum" displays binding properties and, depending on the composition, exhibits hydraulic properties (like a lime-ash binder) or properties of an air binder (like gypsum). In the second case, gypsum is the main cementing phase of the composition, but fly ash and calcite are not just aggregates because in a finely ground state they affect the mixture binding properties.

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SYNTHESIS OF NANOCRYSTALLINE $Y_2Zr_2O_7$ USING MECHANICAL ACTIVATION

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Zirconates of rare-earth elements and yttrium due to their structure and unique physical and chemical characteristics are considered as promising materials for thermal barrier coatings, catalysts, sensors, ionic conductors, as well as matrices for immobilization of radioactive waste. Recently, much attention has been paid to the improvement of methods for preparation nanocrystalline ceramics based on zirconates. These ceramics have several advantages over microcrystalline ceramics: lower thermal conductivity, higher resistance to radiation, and higher oxygen-ion conductivity [1].

In this work, nanocrystalline yttrium zirconate $Y_2Zr_2O_7$ (fluorite structure) was prepared by two methods using mechanical activation (MA): 1) solid phase synthesis and 2) co-precipitation of hydroxides. ZrO_2 and Y_2O_3 were used as reagents in the solid phase synthesis. The hydroxide precursor was prepared by co-precipitation from a combined solution of zirconium oxychloride and yttrium nitrate with the addition of ammonia solution. MA of the precursors was carried out in AGO-2 laboratory planetary ball mill. The stoichiometric mixture of Zr and Y oxides was mechanically activated at a centrifugal factor of 40 g for 10 min using steel vials and balls. MA of the hydroxide precursor was carried out using zirconia vials and balls at a centrifugal factor of 20 g for 30 min. To complete the synthesis, both precursors were calcined for 3 hours at various temperatures. Nanocrystalline $Y_2Zr_2O_7$ was prepared by calcination of the precursors in the 1000-1200 °C temperature range. The crystallite sizes we evaluated using Scherrer method. It was shown that the specific surface area of $Y_2Zr_2O_7$ powders prepared from the mechanically activated hydroxide precursor was several times greater than that in the case of synthesis without MA under similar conditions. This can be explained by the increased homogeneity of the precursor due to MA and, consequently, by the uniform crystallization of yttrium zirconate during calcination. The increased specific surface area is necessary to improve the sinterability of zirconate powders and to produce denser and more efficient ceramics with a homogeneous microstructure.

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SYNTHESIS OF Ce-CONTAINING SOLID SOLUTIONS BASED ON ZIRCON USING MECHANICAL ACTIVATION

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The development of the nuclear industry is accompanied by a constant increase in the amount of radioactive waste and, accordingly, by the need to recycle it as completely as possible. The most dangerous radioactive waste is long-lived actinides. Zircon $ZrSiO_4$ due to its high chemical, mechanical, and thermal stability [1,2] is one of the most promising matrices for the immobilization of these radioactive wastes. When studying the accumulation of actinides by zircon, cerium is used as an analog of plutonium, since the ionic radii of Pu^{4+} (0.96 Å) and Ce^{4+} (0.97 Å) are close.

The aim of this work is to study the effect of mechanical activation (MA) and the conditions of subsequent calcination on the solid-phase synthesis of zircon-based cerium-containing solid solutions. E.G. Avvakumov et al. [3] have shown that the temperature of solid-phase synthesis of zircon can be substantially reduced by applying a preliminary MA of zirconium and silicon oxides in a centrifugal-planetary mill. The highest zircon yield was achieved in the case of a mixture containing only one hydrated oxide. A mixture of reagents, ZrO_2, $SiO_2 \cdot xH_2O$, and CeO_2, with mole ratio Si:Zr:Ce = 1:0.9:0.1 was mechanically activated in an AGO-2 laboratory centrifugal planetary mill for 10 min at a centrifugal factor of 40 g. The mechanically activated mixture was calcined at various temperatures in the range from 1200 °C to 1500 °C for 3 h. It is shown that the proposed virtually waste-free method for the synthesis of $Zr_{1-x}Ce_xSiO_4$ solid solutions makes it possible to prepare ceramic matrices with a Ce content of 4-5 at.% at a temperature of 200-400 °C lower compared to known methods [2,4].

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SYNTHESIS OF COMPOSITE NICKEL–NANODISPERSED BORON COATINGS

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This work studies the effect of the composition of electrolytes with additives of nanodispersed amorphous boron powder on the boron content in composite electrochemical Ni-B coatings (CECs) as promising high–energy materials. High–energy properties of such coatings are due to the reaction of nickel boride Ni_3B formation as a result of interaction between nickel and boron with release of much heat energy. The optimum percentage ratio of components in a composite is 75 at.% Ni to 25 at.% B.

Ni CECs were obtained from a sulfamate nickel plating electrolyte and electrolyte based on the choline chloride–ethylene glycol deep eutectic solvent (DES). Boron was introduced into electrolytes in the form of nanodispersed amorphous boron powder with the average particle size of about 80 nm and the solution was stirred until a suspension was formed. For these electrolytes, the dependence of the boron content in Ni-B CECs on the boron powder content was established.

It was determined that an increase in the boron powder content to 20 g/l in the sulfamate electrolyte resulted in an increase in its content in Ni-B CECs to 10.4 at.%. Further addition of boron to the electrolyte caused no increase in the boron content in the coating.

Unlike the sulfamate electrolyte, the DES-based electrolyte allows obtaining more boron-rich Ni-B CECs, up to 30 at.% B and more, which is probably due to the high viscosity of this electrolyte resulting in better stability of the suspension. Moreover, the dependence of the boron content in Ni-B CECs on its content in the electrolyte is practically linear in a wide range of boron contents in the electrolyte (0-60 g/l).

Thus, we can conclude on the basis of the obtained results that the choline chloride–ethylene glycol DES electrolyte is very promising for synthesis of high-energy Ni-B CECs, as its application allows providing the optimum nickel/boron ratio in the coating, at which the reaction of their interaction is most efficient.

MECHANOCHEMICAL ACTIVATION AS A FABRICATION METHOD OF CALCIUM PHOSPHATES POWDER MIXTURES FOR 3D PRINTING OF BIORESORBABLE CERAMICS

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Ceramic materials based on calcium pyrophosphate with a given architecture of macropores are some of the promising materials for bone tissue regeneration. The stereolithographic 3D printing is optimal method for macroporous material fabrication, since traditional methods do not allow to control the final structure of the material. In order to obtain 3D structures with high space resolution we used suspensions containing powder mixtures with certain particle size, which were created by mechanochemical activation approaches.

The powder mixture was obtained by milling of hydroxyapatite and monocalcium phosphate monohydrate under a layer of acetone for 15 minutes at a speed of 7000 rpm in a ball mill. As a result, according to XRD amorphous monetite was formed. Also as the result of mechanical activation small powder particles were obtained, which contributes to the effective sintering of ceramics. Dense ceramics was made by molding paste containing the obtained powder mixture, followed by heat treatment at different temperatures. The compressive strength of the dense ceramics up to 154 ± 17 MPa and the Young's modulus up to 8.5 ± 2.0 GPa, it means that the materials will not shield the mechanical load.

Macroporous ceramics were produced by stereolithographic printing followed by heat treatment, during which the polymer component of the material was removed and the ceramics was sintered. For this aim, the powder mixture after milling was sieved through a sieve to reduce the average particle size, mixed with a commercial available acrylic monomers and oligomers and surfactants in various mass ratios. The Jacobs equation was used to approximate the dependence of polymerization depth on the irradiation dose to select the printing mode. As a result of printing, Kelvin structures with pre-designed macroporosity of 60, 70% were produced. The mode of further heat treatment was chosen according to the differential curve of thermal analysis to prevent cracking during polymer decomposition. The obtained macroporous ceramics has compressive strength up to 5 MPa at porosity 60% and up to 1 MPa at porosity 70%, which is enough for medical application.

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MECHANOCHEMICAL SYNTHESIS OF Pb_2MgWO_6 PIEZOCERAMICS DOPED WITH Li UNDER VARIOUS FIRING TIME

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In this study, the synthesis of Pb_2MgWO_6 (PMW) piezoceramics doped with Li_2CO_3 1% and 2% wt. above stoichiometry is investigated. The synthesis was carried out using high-energy mechanochemical activation (m/a) on an AGO-2 mill followed by firing in a PVK-1.4-8 furnace at 750 °C for 2, 4, 6 and 10 hours. Li_2CO_3 was introduced to reduce the electrical conductivity of ceramics and to study its effect on the structure and density. Sintered samples prepared for subsequent polarization must have a high density of more than 90% of the theoretical density, otherwise they will not polarize.

Previously, we obtained PMW samples without the introduction of Li_2CO_3 from the oxides of the respective metals and with the use of precursor $MgWO_4$ [1]. In both cases the samples had a cubic structure with S.G. Fm-3m and a density of about 90%. The densest oxide sample, 8.52 g/cm^3, was obtained after firing at 900 °C and 8.46 g/cm^3 after firing at 700 °C using precursor. Doping the PMW system with lithium carbonate resulted in a decrease in firing temperature from 900 °C to 700 °C and an increased the density of samples containing 1% wt. Li_2CO_3 (about 93%) and a slight decrease in the density of samples containing 2% wt. Li_2CO_3. At the same time the structure modification is preserved. In both the samples synthesized from oxides and using the precursor, the maximum density is 8.63 g/cm^3 and was achieved after firing at 700°C at 1% wt. Li_2CO_3. In the case with 2% wt. Li_2CO_3 the density decreases to 8.33 g/cm^3. Taking into account that the density of the samples increased up to 700 °C when the sintering temperature was increased and started to decrease from 800 °C, it was decided to investigate the effect of firing duration on the density of ceramics at a sintering temperature of 750 °C. Thus, after firing for 2 hours with 1% wt. Li_2CO_3, a ceramic with a density of 95% of the theoretical density was obtained. The samples obtained from the oxides have a density of 8.71 g/cm^3, from the precursor 8.84 g/cm^3. The remaining samples obtained at a firing time of 4-10 hours have a lower density.

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MECHANOCHEMICAL SYNTHESIS OF COBALT-COPPER OXIDE CATALYSTS FOR THE DECOMPOSITION OF HYDROCARBONS

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Mechanochemical activation (MCA) is widely used in various fields of science. For example, with the help of MCA it is possible to prepare the catalysts for the decomposition of hydrocarbons, to synthesize pharmaceutical products and different organic substances without use of catalysts [1]. It is known that catalysts based on metals of the iron subgroup (Fe, Co, Ni) are the most effective in the catalytic pyrolysis of hydrocarbons with formation of carbon nanomaterials (CNMs) [2]. The objective of this work was to elaborate the MCA-based synthetic procedure for obtaining the cobalt-copper oxide catalysts and to study their catalytic performance in decomposition of C_2-C_4 hydrocarbons with the CNM production.

The planetary mill "Activator 2S" was used to prepare the series of CoO-CuO/Al_2O_3 catalysts. During the synthesis of the samples, such parameters as the activation time, the diameter of the grinding balls, and the ratio of the active component to the textural promoter were varied. The report will show the effect of synthetic parameters of MCA procedure on the phase composition of catalyst samples and their catalytic activity in catalytic pyrolysis of hydrocarbons with the production of carbon nanofibers (CNF). The structural features and morphology of the produced CNF material (Fig. 1), depending on MCA parameters of synthesized catalyst samples, will also be presented and discussed.

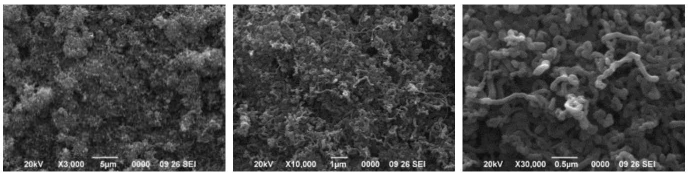

Fig. 1. Structure of carbon product obtained by decomposition of C_1-C_4/H_2 reaction mixture on CoO-CuO/Al_2O_3 catalyst at 650 °C for 2 h. SEM data.

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STUDY OF THE STRUCTURE AND PHASE TRANSITIONS IN α-Fe2O3 HEMATITE DURING MECHANICAL PROCESSING IN A BALL MILL

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Iron oxide, α-Fe_2O_3, is a technologically important material that is widely used as a starting powder for obtaining ferrimagnetic compounds, etc. [1]. Previously, it was shown that α-Fe_2O_3 can partially or completely undergo phase transformations into Fe_3O_4 during mechanical processing in ball mills, depending on the grinding modes [2]. Fe_3O_4 is considered as a very promising material for a new generation of biosensors, contrast agents for magnetic resonance imaging, and also as a chemical catalyst and an integral part of drugs.

The aim of this work was to study the phase transformations in α-Fe_2O_3 during its mechanical grinding in an AGO-2S ball mill by X-ray phase analysis. Processing was carried out using steel balls (diameter 6 mm) under various conditions, including time (up to 120 minutes), grinding medium (water, isopropyl alcohol, air) and mill rotation speed (1290, 1820, 2220 rpm). The obtained samples were studied by X-ray phase analysis on an ARL X'tra diffractometer.

Regularities of phase transformations in α-Fe_2O_3 depending on processing modes were established. It is shown that significant phase transformations α-$Fe_2O_3 \rightarrow Fe_3O_4$ during grinding of hematite occur at a high speed of rotation of the mill. At the same time, with increasing treatment time, the concentration of the formed magnetite phase increases and amounts to 98 wt.% with a treatment time of 120 minutes. Also, the processing environment plays a decisive role in the phase transformation of the original iron oxide.

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MICROSTRUCTURE AND MECHANICAL PROPERTIES OF AN ALUMINUM QUASICRYSTAL-FORMING ALLOY PRODUCED BY UNIAXIAL HOT COMPACTION AND ADDITIVE MANUFACTURING

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This work aims to compare the microstructure and mechanical properties of a quasicrystal-forming $Al_{95}Fe_2Cr_2Ti_1$ alloy manufactured by uniaxial hot compaction (UHC) and selective laser melting additive manufacturing (SLM-AM). To produce the UHC and SLM samples, the process parameters were optimized first. Then, microstructural characterization has been performed by a combination of Scanning Electron Microscopy, X-ray Diffractometry, and Differential Scanning Calorimetry. Mechanical properties have been investigated by Vickers microhardness and compression tests. Due to the ultra-rapid cooling rate and ultra-high temperature gradient during SLM process, the fine grains and ultra-fine dispersed QC and/or approximant phases in the SLMed sample significantly improve its mechanical properties. The microstructure of UHC with heterogeneous, coarse, and irregular phases associated with poor bonding of powder particles due to the presence of oxide layers result in premature failure of samples. The fracture stress and strain obtained were 577 MPa and 30% for the UHCed samples, and 792 MPa and 40% for the SLMed samples. The Vickers microhardness of the SLMed samples (269 ± 21) was notably higher than that obtained by the UHCed samples (150 ± 3).

EFFECT OF SCANNING STRATEGY ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF A BIOCOMPATIBLE Ti-35Nb-7Zr-5Ta ALLOY PROCESSED BY LASER POWER BED FUSION

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Biocompatible beta-TiNb alloys have been considered promising to replace the more established Ni-Ti and Ti-6Al-4V alloys used in implants because of their lower Young's modulus and excellent biocompatibility. In this study, the influence of the scanning strategy on the microstructure and mechanical properties of a beta Ti-35Nb-7Zr-5Ta (TNZT) alloy processed by laser-powder bed fusion (L-PBF) is investigated for the first time. Three scanning strategies were considered: unidirectional-Y; bi-directional with 79° rotation (R79); and chessboard bidirectional and 90° rotation between islands (CHB). The highest relative density was obtained for samples produced using the CHB and R79 strategies. The unidirectional-Y strategy presented a lack of fusion between layers, which resulted in a lower elastic modulus. The scanning strategies directly influenced the crystalographic texture with the unidirectional-Y strategy resulting in a material with the strongest texture and lower average aspect ratio of the grains. The R79 sample showed the highest yield strength among all samples.

Keywords: Laser-powder bed fusion; Beta Ti-alloys; Additive manufacturing; Scanning strategy

ALLOY DESIGN FOR MICROSTRUCTURAL-TAILORED BORON-MODIFIED FERRITIC STAINLESS STEEL TO ENSURE CORROSION AND WEAR RESISTANCE

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This study proposes the development of functionalized stainless steel with balanced corrosion and wear resistance from boron-modification of AISI 430 ferritic stainless steel, using spray forming as processing route. The wear resistance was investigated through a plate-on-cylinder wear test in water-based drilling mud, which was designed to simulate in laboratorial scale the tribosystem found in the wear of risers and casings used in deep water oil exploitation. The corrosion assessment includes potentiodynamic polarization and electrochemical impedance spectroscopy in 0.27 M KCl solution, since KCl is used as clay swelling inhibitor. For comparison purposes, API 5L X80 steel was also included, once this material is used in risers and casings manufacture. It was shown that the addition of boron (1.2 and 3.5 wt.%) led to the formation of microstructures composed of an α-ferrite matrix with homogeneously distributed M_2B-type borides of different morphologies. Electrochemical tests revealed high corrosion resistance of the alloy with 1.2 wt.% B. However, the alloy with 3.5 wt.% B showed a considerable decrease in corrosion resistance due to Cr-depletion of the ferritic matrix given the M_2B formation richer in Cr. The increase of B content was always accompanied by an improvement in wear resistance. It was observed that the alloy with 1.2 wt.% B displays the better combination of corrosion and wear resistance. Therefore, it was shown that the corrosion-wear resistance of AISI 430 stainless steel may be improved by designing appropriate boron-modified stainless steel compositions, being an interesting route to design corrosion and wear resistant steels to endure to the harsh environment and operating conditions found in the oil and gas industry.

TWO-LEVEL MODEL OF COMPOSITE SYNTHESIS ON A SUBSTRATE FROM POWDER MIXTURE TiO_2-Al

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By definition, the reaction rate is the change in the level of completeness of the reaction over time. It was this way with the introduction of the formal-kinetic description of the evolution of the degree of transformation that allowed many qualitative regularities of the synthesis of new materials to be established in macrokinetics. However, at present, there is a need to build models that take into account the processes occurring at different scale levels.

Thus, in accordance with literature data, for a mixture of Al and TiO_2 powders, we can limit ourselves to the analysis of two total reactions:

$$4Al + 3TiO_2 \rightarrow 2Al_2O_3 + 3Ti \ (1) \text{ and } 3Al + Ti \rightarrow Al_3Ti \ (2).$$

In general, the sequence of reactions in this system depends on the ratio of components and the process temperature. However, the phase composition (Al_2O_3 and Al_3Ti) in the final product is the same in most cases. Total reactions (1) and (2), actually proceed in several elementary stages, among which is diffusion

In the macroscopic description of the synthesis of composites, the peculiarities of the accompanying processes are taken into account through kinetic functions. In two-level models, when introducing the concept of an equivalent medium or so-called reaction cells, the diffusion-controlling phenomena are taken into account explicitly. In contrast to macrokinetics models with separation of reaction cells, our model takes into account thermo-chemo-mechanical phenomena on different scales. Thus, thermal stresses are directly related to the heating of a macro sample by a moving heat source. The effective properties of the macro-sample, the total chemical heat release and the second kind stresses are considered as a consequence of the processes leading to changes in the composition and structure and "proceeding" at a lower scale level.

This approach also has a thermodynamic justification [1].

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INFLUENCE OF HEAT LOSS AND KINETIC FUNCTION TYPE ON COATING SYNTHESIS DYNAMICS UNDER MOBILE SOURCE CONTROL

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This paper presents a one-dimensional model of thermal treatment of a powder layer by a scanning laser beam taking into account the chemical heat source. It is assumed that the powder mixture contains chemically interacting components, and the whole complex of chemical reactions is described by the total scheme "reagent - reaction product". The peculiarities of reactions in powder systems are taken into account through the kinetic function. A change in the form of the kinetic function can be associated with the pre-activation of powders, which is partly used in 3D technologies to improve the wettability of the refractory component by the fusible one in the synthesis of composites, as well as to realize the formation of strengthening particles in these conditions in mixtures that are far from stoichiometry.

Additionally, the model takes into account heat loss by convection, which plays an important role in laser technology.

The melting dynamics, peculiarities of the reaction zone and temperature field under varying parameters of the external heat source are analyzed.

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THE INFLUENCE OF MECHANICAL ACTIVATION ON THE COMPOSITION OF THE LEAD THIOSULFATE DEGRADATION PRODUCTS

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An insignificant (about 5-10%) amount of the supplied mechanical energy is initially converted into chemical energy during mechanochemical activation. The rest and part of the relaxed initial energy are released as heat. Not only the speed, but also the possibility of the reaction and the route of the reaction under the conditions of mechanochemical action on the reagent depends on energy released per unit of time.

To study the effect of the intensity of the mechanochemical treatment upon the transformation, the decomposition reaction of lead thiosulfate was chosen. For the thermal decomposition of this substance at the temperature range up to 250 °C, gaseous and solid products are known. As a complicating factor, the reaction of the primary transformation may be accompanied by a secondary reaction of the interaction of solid products in the temperature range above 400 °C.

Mechanochemical treatment was carried out at the AGO-2 planetary mill, the reactors-drums and grinding bodies-balls are steel, the diameter of the balls – 3-4 mm, loading the drums 1:40 with the substance and grinding bodies. The impact of grinding media was characterized by their acceleration in the mill drum by values of 20, 40 and 60g. The temperature of the external coolant was measured at the inlet and outlet of the activator.

The dependences of the degree of conversion of lead thiosulfate from the conditions of mechanical activation are obtained. At accelerations of grinding media 20g, the reaction remains at the stage of increasing the reactivity of the product; exposure to 40g leads to direct decomposition; exposure to grinding media 60g most likely causes a secondary reaction of the interaction of solid products of sulfide and lead sulfate. Certain heat dissipation capacities correspond to the values of 63, 543, 1463W for conditions 20, 40 and 60g of mechanochemical treatment.

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Cu-Al ALLOYS OBTAINED BY SPARK PLASMA SINTERING OF POWDER BLENDS AND MECHANICALLY ALLOYED MIXTURES

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Spark plasma sintering (SPS) is an advanced sintering method, the essence of which is consolidation of powders in a die under uniaxial pressure and pulsed direct current. Processing the powders by SPS allows conducting alloying and densification in a single technological step. The alloy formation at the contacts between the particles of different metals can be accelerated owing to a local rise in temperature in those regions under a passing electric current.

In this work, we report the alloy formation in the Cu-10 wt.% Al system upon SPS of the powder blends. Two aluminum powders differing in the particle size were used for preparing the blends. For a comparative analysis, bulk alloys were also obtained by SPS of mechanically alloyed powders of the same composition. Mechanical alloying of the mixtures was conducted in a high-energy planetary ball mill. The product of mechanical alloying consisted of a Cu(Al) solid solution as a major phase and the Cu_9Al_4 intermetallic as a minor phase.

It was found that the mechanically alloyed powders required higher temperatures to be consolidated by SPS to nearly full density than the blended powders (~800 ºC versus ~500 ºC). During SPS of the blends, partial alloying between the metals occurred. In the materials obtained by SPS of the blends at 480 ºC (holding time 5 min), the aluminum particles were covered with a double-layer shell consisting of the Al_2Cu and Cu_9Al_4 intermetallics. The bulk materials obtained by SPS of the product of mechanical alloying were single-phase Cu(Al).

The phase composition, microstructural features and properties of the alloys obtained by SPS of the blends and mechanically alloyed mixtures will be comparatively analyzed in this presentation.

EFFECT OF SURFACTANTS ON MECHANICAL ACTIVATION AND SYNTHESIS IN THE TITANIUM - GASEOUS NITROGEN SYSTEM: MORPHOLOGY AND PHASE COMPOSITION

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Mechanical activation (MA) leads to the formation of agglomerates consisting of particles of starting components. As the MA time increases, the agglomerates become denser, which complicates the nitridation process. The introduction of surfactants can decrease agglomeration and improve the formation of nitride.

MA of titanium powder (≤ 100 μm) was performed in a M-3 planetary mill in the nitrogen atmosphere at a pressure of 4 * 105 Pa with the addition of a surfactant (solid stearic acid, 0.05-10 wt%). The phase composition was characterized by X-ray diffraction (DRON-3), and morphology and dispersion of powders were examined by scanning electron microscopy (QUANTA 200 3d and Philips SEM515). Figure 1 shows the morphology at different MA times and proportion of surfactants.

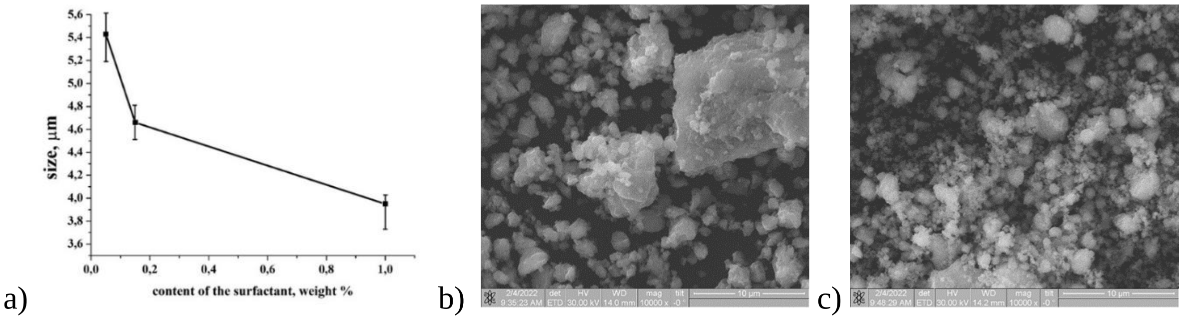

Fig. 1. The average particle size of titanium after 25 min MA in nitrogen as a function of surfactant proportion (a), SEM image of titanium powder after MA: 25 min MA + 1.0 wt % surfactant (b), 40 min MA + 0.5 wt % surfactant (c).

The introduction of surfactants was found to decrease the period for formation of titanium nitride. In this case, the minimum time of complete nitridation is 25-30 min MA, and the proportion of surfactant is 1.5 wt%. The addition of surfactant significantly reduces the number of large fractions, resulting in a decrease in the average size of solid-phase particles. The optimal technological modes of mechanochemical synthesis of titanium nitride were found.

The research was done using equipment of Tomsk Regional Core Shared Research Facilities Centre of National Research Tomsk State University. This work was funded by the Russian Science Foundation (Grant No. 22-23-00106).

EVOLUTION OF TITANIUM POWDER MORPHOLOGY DURING MECHANICAL ACTIVATION IN NITROGEN

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Titanium nitride is a promising material due to a combination of mechanical, thermal, and physical and chemical properties. Mechanical activation (MA) can be used to obtain nitride phases by grinding titanium in nitrogen [1]. In this work, MA of titanium powder (≤ 100 μm) was performed in an M-3 planetary mill in the nitrogen atmosphere at the pressure of $4*10^5$ Pa within 10-60 min. The phase composition was characterized by X-ray diffraction (DRON-3), the specific surface area was determined by the BET method, and the morphology and dispersion of powders were examined by scanning electron microscopy (QUANTA 200 3d (USA) and Philips SEM515 with EDAX spectrometer). Figure 1 shows the evolution of titanium powder morphology as a function of the MA time in nitrogen.

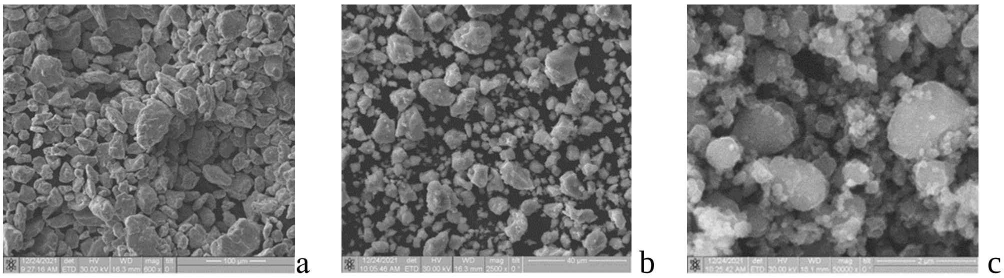

Fig. 1. SEM image of titanium powder after: 10 min MA (a), 40 min MA (b), 60 min MA (c).

MA of titanium powder in nitrogen was found to initiate mechanochemical synthesis and leads to the formation of nanostructured agglomerates of titanium nitride. The interaction of titanium powder with nitrogen starts after 10 min MA. and after 40 min. The complete conversion of the reactants into titanium nitride occurs after 40 min MA. The increase in the lattice microdistortions in titanium with the formation of a nanostructure during MA, along with the growth of the interfacial surface, also contributes to the process of nitridation.

The research was done using equipment of Tomsk Regional Core Shared Research Facilities Centre of National Research Tomsk State University. This work was funded by the Russian Science Foundation (Grant No. 22-23-00106).

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OPTIMIZATION OF LLZ SOLID ELECTROLYTE TRANSITION FROM TETRAGONAL MODIFICATION INTO CUBIC USING MECHANOACTIVATION

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Lithium-conducting $Li_{7-3x}Al_xLa_3Zr_2O_{12}$ solid electrolyte with a garnet structure is currently the most studied structural type among solid electrolytes with high Li^+-conductivity. Earlier, the features of the formation of cubic modification of solid electrolyte of the composition $Li_{6.4}La_3Al_{0.2}Zr_2O_{12}$ (c-LLZ) were studied [1]. Mechanical activation can increase the dispersion and reactivity of powders, lower the temperature and duration of synthesis and lead to the formation of c-LLZ under milder conditions [2].

The aim of the work is to study the effect of mechanical activation on the formation of powdered c–LLZ in the process of solid-phase synthesis using low-melting crystallohydrates.

The composition of the charge was calculated according reaction:

$$3.2Li_2CO_3 + 3La(NO_3)_3{\cdot}6H_2O + 2ZrO(NO_3)_2{\cdot}2H_2O + 0.2Al(NO_3)_3{\cdot}9H_2O \rightarrow Li_{6.4}La_3Al_{0.2}Zr_2O_{12}$$

After the 1st stage of the charge components interaction at 900^oC, the charge was melted, followed by the decomposition of nitrates and the formation of a sinter consisting of 2 modifications of LLZ: tetragonal (PDF 01-080-6140) and cubic (PDF 01-080-7219) in commensurate quantities. The presence of tetragonal modification leads to a decrease in the Li^+-conductivity of LLZ solid electrolyte. Further, the mechanical activation of the sinter was carried out using AGO-2C planetary mill in 4x1 min mode with a centrifugal factor of 20g using zirconium dioxide vials and balls. The balls : load mass ratio was 20:1. Mechanically activated LLZ powder (d=0.3-0.4 μm) was sintered at 1000^oC (heating rate of 10^oC/min) for 2 and 4 h. According to X-ray phase analysis, it was found that when the powder is sintered at 1000^oC for 4 h, a complete transition from LLZ tetragonal modification into cubic one occurs. Thus, as a result of mechanical activation, there is a significant decrease in temperature (by 150°C) and duration of preparation LLZ powders with high Li^+-conductivity ($\sigma \sim 2{\cdot}10^{-4}$ S/cm).

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COMPOSITE MATERIALS MODIFIED WITH CARBON PARTICLES PRODUCED BY SHS TECHNOLOGY

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According to the literature data, the formation of nanodispersed particles by the method of self-propagating high-temperature synthesis makes it possible to obtain low-sized particles with properties that differ from those of bulk carbon materials. The resulting nanosized particles have a high adsorption activity, large specific surface area. The conducted studies have shown that, depending on the technology for the formation of these particles in the reactor, it is possible to control the morphology and lateral sizes of the particles, which in the future will make it possible to purposefully change the activity of these particles. The activity of nanosized particles obtained by self-propagating high-temperature synthesis is due to the imperfection of the formed nanocrystals. It is shown that, depending on the methodology for the formation of carbon particles, various structures are formed with characteristic properties inherent only to them. Thus, the formation of diamond-like structures, fullerenes, fullerites, carbon nanotubes, rods, disks, graphenes, etc. is possible. These materials differ significantly in properties from each other. The disadvantage of the considered technologies is, in most cases, the high cost of the obtained particles, as well as the low yield of carbon nanocluster structures. In some cases, environmentally harmful technologies are used. In this connection, the use of the technology of self-propagating high-temperature synthesis will make it possible to obtain carbon nanoparticles of various nomenclature in large quantities. The use of the SHS method will make it possible to obtain nanosized cluster structures not only of carbon, but also from materials consisting of other chemical elements of the periodic system. In the course of the conducted studies, it was found that as a result of the use of self-propagating high-temperature synthesis for the processing of organic raw materials, particles of the nanometer range with different dispersion distributions are formed. The dispersity of the studied samples depends on the organic raw materials used. The introduction of carbon nanosized particles into the polymer matrix at concentrations of 1-3 wt.% increases the tensile strength of the composite material by 26-34%. This effect is explained by the formation of a network of labile physical bonds between modifier molecules and polymer molecules. Exceeding the specified concentration leads to a decrease in strength characteristics.

MECHANOCHEMICALLY-ASSISTED SYNTHESIS OF Cu-Ag MICROFLAKES

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Nano- or microsized metals have been widely used as conductive fillers in conductive inks and pastes. Ag is the most common metallic filler because of its low resistivity, however, the problems of electromigration and high cost of Ag prompt the search for alternatives to it. Cu could replace Ag as the metallic filler but it is prone to oxidation, resulting in the decrease in conductivity. To overcome these drawbacks, Ag-coated Cu powders and Cu−Ag alloy have been applied as conductive fillers [1]. The paste filled with Ag-coated Cu was shown to have higher electrical conductivity with better stability than Cu-based paste [2]. Apart from that, the flake morphology, as compared with the spherical morphology, is preferable for obtaining better electrical conductivity which is due to a larger contact area between neighboring flakes and denser packing of the flakes in the printed layer. Therefore Cu-Ag alloy microflakes could be a promising candidate to apply to conductive pastes for flexible printing electronics.

In this work, a simple, inexpensive, and eco-friendly synthesis method of Cu−Ag microflakes has been developed. Firstly, Cu nanoparticles were synthesized be the reduction of copper nitrate in ethylene glycol at 180 °C in the presence of NaOH. The as-synthesized Cu powder was then dispersed in a mixture of ethyl alcohol and a dispersant followed by the mechanochemical treatment of the dispersion in a ball mill resulting in the formation of Cu flakes of approximately 50–70 nm thick, 1–2 μm long and 1 μm wide. Next, by adding $AgNO_3$ dissolved in H_2O into the Cu particle dispersion, the alloy Cu−Ag microflakes were prepared. The morphology and size of the particles so prepared were investigated by X-ray phase analysis, electron microscopy and thermogravimetric analysis. It was shown that the Cu−Ag alloy particles were also flake-like in shape and similar in size to the original Cu microflakes. The effect of synthesis conditions, such as synthesis time, Ag precursor concentration, silver-to-copper molar ratio, and parameters of mechanochemical processing on thickness, size and uniformity of the alloyed microflakes was studied. The results obtained in this study were compared with those obtained by wet chemical synthesis alone. The flake-like Cu-Ag particles are supposed to be used in manufacture of conductive pastes for printing electronics.

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FABRICATION BY INKJET 3D-PRINTING AND INVESTIGATION OF THE MICROSTRUCTURE OF A PLANAR NiO/CGO COMPOSITE ANODE FOR A SOLID OXIDE FUEL CELL

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In the last decade, 3D printing of SOFCs has been actively developed making it possible to reduce the number of technological stages of production, to improve electrochemical characteristics of SOFCs and their geometry and microstructure, and thus resulting in the formation of a unique texture and shape of the final product.

The aim of this work was to fabricate a planar SOFC anode based on the NiO/$Ce_{0.8}Gd_{0.2}O_2$ composite using a unique method combining direct layer-by-layer inkjet printing with selective laser sintering, integrated into a laboratory 3D printer [1].

The new paste compositions for 3D printing were prepared using liquid grinding in a ball mill. Effects of the organic components and the parameters of mechanochemical processing on the rheological characteristics of the paste were investigated. The optimal paste composition for 3D printing has been found.

In order to optimize the annealing mode of the anode blanks, the final temperature of treatment was varied from 1300°C to 1400°C, while the heating rate and the intermediate temperature for annealing the main organic components of the paste were varied in the range of 1–2 °C/min and 300–500 °C respectively. The degree of deformation and microstructure of the printed anodes after sintering, depending on the method of their formation (tape casting or inkjet printing), the parameters of heat treatment and laser sintering power, were investigated.

The optimum annealing temperature regime (1400 °C, 1 °C/min) allows avoiding the sample deformation during sintering, while the use of laser treatment at the stage of the sample formation allows the formation of a complex surface with a wide size distribution of the pores. The samples with a minimum deformation have been reduced in a hydrogen flow, and the porosity and electrical conductivity of the NiO/CGO composite anodes were studied. The porosity of the composite anodes was comparable to the data reported in the literature [2], while the electrical conductivity of the anode after laser treatment was found to increase twice.

This research was funded by the state assignment to ISSCM SB RAS (Project No. 122032900069-8).

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MECHANICALLY STIMULATED REACTION VELOCITY REGULATION IN HIGHLY THERMITE MIXTURES APPLYING STEP-BY-STEP PRECURSOR FORMATION

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The aim of mechanochemical formation of ferrite $MgFe_2O_4$ particles in industrial scale for functional materials may be achieved applying thermite reaction in Fe_2O_3/Mg and Fe_2O_3+MgO mixtures. But it needs slowing the velocity of component~~s~~ interaction to prevent components splashing. We applied recently developed approach that we used for reactive systems Fe_2O_3/Me (Me=Al, Zr, Fe) [1-3] where the degree of the interaction was controlled by applying diluted mechanosynthesized precursors Me/Fe having distributed areas of local interaction between highly and slowly reactive components.

The influence of the forming local structure of the particles during the mechanical pre-activation of Fe/Mg and Fe_2O_3/(Fe, Mg) powder precursor on the ferrite output at annealing had been investigated by XRD, SEM and Mössbauer spectroscopy.

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RECYCLING OF WASTE FROM SPARK PLASMA SINTERING OF POWDER MATERIALS BASED ON ZIRCONIUM DIBORIDE

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For sintering ceramic products, it is effective to use spark plasma sintering (SPS), which makes it possible to obtain high-density refractory materials within several minutes at relatively low consolidation temperatures. SPS is used for sintering ultra-high temperature ceramics, for example, based on zirconium diboride [1]. However, this technology does not allow obtaining products of complex geometric shapes with height differences. Therefore, to obtain complex shapes, mechanical processing of the sintered blanks such as electrical discharge machining or high-speed milling is used. The mechanical processing generates waste of the original material of the blank. High-temperature ceramics and hard alloys are expensive materials; therefore, the purpose by this work is to develop a method for processing waste by grinding using a TsEM-7-1 flow centrifugal mill [2] and to study the possibility of using waste for repeat spark plasma sintering of products.

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TRANSITION METAL MONOALUMINIDES STRENGTHENED WITH ALUMINUM OXIDE

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The transition metal aluminides, such as iron, nickel, niobium, cobalt, titanium and others, are promising heat-resistant structural materials for the production of parts of aircraft gas turbine engines, high-temperature fasteners, injection molding units, pumps, dies, bearings, heating elements, tooling for aluminum casting. The strength of the aluminides decreases at temperatures above 600 °C, while corrosion resistance is maintained. To increase the resistance of the material to high-temperature creep, ceramic particles are used as a strengthening phase. However, the cohesive strength of composites based on aluminides is limited by the low wettability of most strengthening phases with intermetallides. The solution to this problem becomes possible if a stable ceramic phase of aluminum oxide is formed simultaneously during the mechanochemical synthesis of iron, nickel and other metals. In this case, high-energy systems become promising for mechanochemical synthesis, among which the greatest thermal effects are observed for reactions of reduction of metal oxides by aluminum, during which aluminides and aluminum oxide are formed as the main phases.

Using X-ray diffraction analysis, IR and Mössbauer spectroscopy, it was shown that the monoaluminides of iron, nickel and copper, strengthened by aluminum oxide particles, are formed during mechanostimulated reduction reactions of these metal oxides by a twofold excess of aluminum.

The work was carried out within the framework of the state task of the ISSCM SB RAS (Project No. 121032500062-4).

ALUMINA-ZIRCONIA CERAMICS CONTAINING CERIA AND CALCIA

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The formation of hexaaluminates of different chemical compositions in alumina-zirconia ceramics increases their fracture toughness [1]. Comparative studies of the formation of various hexaaluminates, including ceria and calcia, are practically non-existent in the literature. Simultaneously, works devoted to the synthesis of these compounds in alumina zirconia and alumina matrixes have been performed on this day [2, 3].

In this study, suspensions were prepared from α-Al_2O_3 and 3Y-TZP powders and dispersed separately in a ball mill. During the mixing stage of the suspensions, additives of ceria and calcia were added in various amounts. Pressing and sintering of the materials was carried out. Also, mixtures without zirconia were investigated to assess changes in the phase composition during heating. Density, porosity, microstructural studies were evaluated. The phase composition and mechanical properties of the materials were studied.

The formation of hexaaluminates during sintering of the materials has been observed. Simultaneously, according to X-ray phase analysis, some additives are consumed for additional stabilization of 3Y-TZP. Reduced density and microhardness of the materials as well as increased fracture toughness have been determined.

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VACUUM-TIGHT WEAKLY CONDUCTIVE CERAMIC MATERIAL

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Strict requirements are imposed on ceramic materials used as an element of a vacuum system, namely, to remove a static charge from the internal structure of the chamber, consisting in measuring the vacuum-tight characteristics of mechanical strength. The electrical conductivity of materials in the range of 10^{-13}-10^{-5} S/cm is usually sufficient to prevent dangerous charge buildup. These characteristics are determined both by the composition of the ceramic material and by the method of its manufacture.

The paper presents a method for obtaining a vacuum-tight low-conductive ceramic material, the fundamental feature of which is the use of precursors prepared by the method of joint mechanical activation in a high-energy planetary mill AGO-3 for 1 min. The production of ceramic samples was carried out by the method of semi-dry pressing, which includes the following operations: preparation of the molding mass, laying it in molds, compaction, stripping, drying, firing, cooling to ambient temperature.

The molding mass was prepared from a powder composition of the following composition, wt %: Al_2O_3 – 61.7; BaO - 18.5; Fe_2O_3 -19.4; Li_2O - 0.4. The composition was mixed with water (molding humidity 9%) and pressed on a hydraulic press at a pressure of 200 MPa. Next, the samples were dried in air for 24 hours, and then in an oven at a temperature of 200°C. After drying, the samples were fired at a temperature of 1600°C. The resulting ceramic samples have the following characteristics: electrical conductivity $1.50\cdot10^{-7}$-$1.05\cdot10^{-4}$ S/cm; helium leakage rate for a test duration of 30 min $< 5\cdot10^{-10}$ mbar·l/s; density 3.75 g/cm^3, compressive strength 590 MPa.

The work was carried out with support within the Federal Targeted Programme according to Agreement No. 075-15-2021-1359 of 13.10.2021 (internal No. 15. SIN.21.0015) and the Ministry of Science and Higher Education of the Russian Federation within the framework of the state task of the Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences (project No. 121032500071-6).

STUDY OF THE POSSIBILITY OF OBTAINING COMPOSITES AlN/Fe USING MECHANOCHEMICAL IMPACT

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In this work, a study of the influence of joint mechanical processing (MP) of aluminum and carbonyl iron nitride powders on the properties of AlN/Fe composites was conducted. The dependence of the change in the structure on the methods of manufacturing composites: pressing and sintering temperature is determined.

The mechanical processing of powders was carried out in the centrifugal planetary mills of the types of AGO-2 and EI with different energy ramps. In the AGO-2 mill, steel balls and drums were used, and in the EI corundum-lined drums and ceramic balls were used. The sintering of compressed composites was carried out in the air at temperatures up to 900 °C.

It was determined that with an increase in the firing temperature of composites, the mechanical processing of which was carried out in an EI mill, the formation of various phases in their structure (Fig. 1) was observed.

700 °C 800 °C 900 °C

Fig. 1. Appearance AlN/Fe of composites.

This work was conducted within the framework of the Institute of Solid State Chemistry and Mechanochemistry SB RAS budget project No. 121032500071-6 and the target Program in accordance with Agreement No. 075-15-2021-1359 of 13.10.2021 (Internal number 15.SIN.21.0015).

SYNTHESIS OF BORNITE FROM ELEMENTS USING MECHANICAL ACTIVATION

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When synthesizing new compounds, it is very important to develop an efficient, technically feasible, environmentally friendly method for the synthesis of compounds with a minimum number of stages. The purpose of this work was the synthesis of pure bornite (Cu_5FeS_4) for further studies of its reactivity with respect to various leaching reagents.

The synthesis of Cu_5FeS_4 included 2 stages. At the 1-st stage, mechanical activation (MA) of a mixture of copper (PMU, 99.99%), iron (PZHR, 99%), and sulfur (Chemically pure) powders was carried out in an AGO-2 planetary ball mill in an argon atmosphere. Steel balls (d=6 mm) were used as grinding bodies. The mass ratio of balls and mixture (Cu, Fe, S) was 10:1. MA was carried out for 10, 15, 20, and 30 min. At the 2-nd stage, these powders were annealed in an argon atmosphere at 400 ºC for 1 h. The synthesized bornite samples were studied using X-ray phase analysis (XRD, Bruker D8 Advance).

XRD results showed that the crystal structure of the products after MA is mainly represented by the covellin (CuS) phase with relflections at $2\theta = 29.3°, 32.3°, 47.9°$ (PDF file #24-60). Also, the diffraction patterns after MA showed peaks of pure copper, iron, and sulfur, the presence of which indicates an incomplete synthesis. On the diffraction pattern of the sample after 30 min of MA, heated at 400 ºC for 1 h, the covellin peaks completely disappeared and reflections at $2\theta = 26.9°, 28.2°, 32.7°, 35.7°, 46.9°$ (PDF file #42 -1405) appeared related to the bornite phase.

Thus, after the mechanical activation of the mixture (Cu, Fe, S), the covellin-iron-sulfur system appears, from which, during annealing at 400 ºC for 1 h, a thermodynamically stable pure Cu_5FeS_4 bornite phase is formed.

The method for obtaining Cu_5FeS_4 presented in this work is simple, does not require the use of solvents and additional reagents, and can be recommended for the preparative synthesis of pure bornite.

INTERACTIONS IN THE $ZnCl_2$ AND LiH MIXTURES UNDER BALL MILLING CONDITIONS

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The development of new methods for the synthesis of metal hydrides, which cannot be obtained by direct hydrogenation (AlH_3, ZnH_2, etc.), is an urgent task. In this regard, metathesis reactions occupy a special place, however, the use of organic solution ("wet") based approaches has a number of significant drawbacks, which are mainly associated with the purification, further removal and regeneration/utilization of the solvent, as well as the solvation of the product [1-2]. A good alternative is to carry out such reactions under conditions of mechanochemical activation [3].

In current research for the synthesis of zinc hydride compounds an anhydrous zinc chloride $ZnCl_2$ (99.95% metal base) as well as lithium hydride (96-97% by gas volumetric analysis). Mechanochemical treatment have been carried out with Retsch MM400 vibrational mill with 25 ml grinding jars and 15-20 g of stainless 55 ø mm stainless balls, 25-45 min grinding duration.

PXRD of the samples with the starting molar ratio of LiH and $ZnCl_2 \leq 2$ exhibit the reflections of LiCl, LiH and metallic Zn, alongside that the content of hydrogen decreases at least at 60%. Once the initial reagents ratio increases up to 4-6 with subsequent addition of zinc chloride up to n(H):n(Cl) = 2-2.5:1 leads to the formation of mixtures with only LiCl reflections and with almost unaltered hydrogen content. The reaction pathway in the second case apparently includes the intermediate formation of complex zinc hydrides Li_xZnH_{2+x}, that among the related systems including polymeric hydrides, have been observed in the synthesis of alane AlH_3 [3].

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MECHANOCHEMICAL SYNTHESIS OF CALCIUM HYDROXYAPATITE WITH SILVER CATIONS

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Synthetic hydroxyapatite – $Ca_{10}(PO_4)_6(OH)_2$ – is widely used in bone tissue engineering due to its similarity in composition to the mineral component of bone, as well as chemical stability, bioactivity and biocompatibility. Currently, the use of implants is steadily increasing, which is associated with an increase in life expectancy. A common problem with surgical intervention associated with implantation is the risk of complications as a result of paraprosthetic infection, which increases the duration and cost of therapy. In addition, an infectious complication can lead to an unfavorable outcome of surgical intervention. One of the common and generally accepted strategies for preventing infections associated with implantation and transplantation is using of materials with antibacterial properties. Silver and compounds based on it are known for high antimicrobial activity due to their antiseptic properties against a number of bacteria.

The purpose of this work was to investigate the possibility of synthesis of hydroxyapatite substituted with silver ions by the mechanochemical method.

The synthesis of samples was carried out in a planetary ball mill AGO-2 by processing of a mixture of reagents for 30 min. in accordance with the equation:

$$6CaHPO_4 + (4\text{-}x)CaO + \frac{x}{2}(Ag_2O) \rightarrow Ca_{10-x}Ag_x(PO_4)_6(OH)_{2-x} + (2+\frac{x}{2})H_2O,$$

where x = 0; 0.2; 0.5.

According to XRD analysis and FTIR spectroscopy, the synthesized powders have the structure of hydroxyapatite. Impurity phases are not observed. The parameters of the crystal lattice depend on the concentration of the introduced substituent. The data obtained indicate that mechanochemical synthesis can be used for the synthesis of silver-substituted hydroxyapatite. Studies have shown that the thermal stability of the obtained compounds depends on the concentration of the substituent. At x = 0.2, the sample remains single–phase up to 600 ^{o}C, and at x = 0.5 up to 400 ^{o}C. At higher annealing temperatures, XDR patterns show reflections of impurity phases of metallic silver and β-tricalcium phosphate. Thus, we can conclude that the use of high-temperature processing in the manufacture of products from synthesized materials is not recommended.

THERMAL STABILITY OF IRON AND SILICON CO-SUBSTITUTED HYDROXYAPATITE OBTAINED BY MECHANOCHEMICAL METHOD

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The synthetic bone materials based on cation-substituted or anion-substituted hydroxyapatite have recently received considerable attention, as the introduction of ions into the apatite structure improves its biological and physicochemical properties. There are very few works on simultaneous cation and anion co-substitution into hydroxyapatite structure. Such substitution allows several different material characteristics to be improved at the same time, which is very important for application of the material.

This work is devoted to the study of the thermal stability of iron and silicate co-substituted hydroxyapatites (FeSi-HA) obtained by the mechanochemical synthesis in AGO-2 planetary ball mill.

A series of FeSi-HA samples with the general formula $Ca_{10-x}Fe_x(PO_4)_{6-x}(SiO_4)_x(OH)_2$, where $x = 0; 0.1; 0.2; 0.5; 1.0; 1.5; 2.0$, was obtained by the fast mechanochemical synthesis within 40 min. It has been determined that the substitution limit for mechanochemical synthesis is $x = 1.5$. At higher concentration, an amorphous phase is formed. The simultaneous introduction of iron and silicon ions in equal concentrations leads to an increase in the unit cell parameter a and a decrease in the parameter c. The crystallite size decreases with increasing concentration of substituents.

The analysis of the behavior of the synthesized powders upon heating showed that the introduction of substituents leads to a decrease in the thermal stability of hydroxyapatite. The release of adsorbed and crystallization water is detected at heating up to 500 °C. The amount of water is increase with the increase of substituent concentration. A partial decomposition of FeSi-HA samples with a release of β-$Ca_3(PO_4)_2$ is observed at 735 °C. For concentration of substituents in the samples higher than $x = 0.5$ further decomposition of FeSi-HA accompanied by segregation of iron oxide Fe_2O_3 at 1000 °C is detected. This leads to the conclusion that the limit of simultaneous substitution in HA for iron and silicon ions is lower than assumed, namely less than $x = 1$.

This research was carried out within a state assignment to the Institute of Solid State Chemistry and Mechanochemistry SB RAS (project No. 121032500064-8).

MECHANOCHEMICAL SYNTHESIS Cu-SUBSTITUTED HYDROXYAPATITE USING DIFFERENT COPPER SOURCES

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Hydroxyapatite is widely used in various fields of medicine and is an inorganic material with a chemical composition of $Ca_{10}(PO_4)_6(OH)_2$. Since the stoichiometric hydroxyapatite has a low rate of bioresorption and does not have antibacterial properties, an appropriate substituent ions are introduced into its structure to impart the necessary characteristics. Materials based on the Cu-substituted hydroxyapatite have antibacterial properties that prevent inflammation and stimulate the growth of the new bone tissue, which is very important when used in surgery.

The aim of the work was to study the process of mechanochemical synthesis of the copper-substituted hydroxylapatite $Ca_{10-x}Cu_x(PO_4)_6(OH)_{2-x}$ with the substitution of calcium cations by copper cations. During the synthesis, different reagents-sources of copper cations were used (Cu, $(CuOH)_2CO_3$, CuO, Cu_2O).

It is shown that when using CuO as a carrier of substituent cations, the substitution limit in the hydroxyapatite structure is found to be $x = 1$. The linear dependence of the unit cell parameter c and its volume on the concentration of the injected dopant is revealed. An increase in the concentration leads to a decrease in volume, which is consistent with a change in the ionic radius when replacing calcium cations with copper cations: $r(Ca^{2+}) = 0.100$ nm, $r(Cu^{2+}) = 0.073$ nm.

The possibility of the mechanochemical synthesis of the copper-substituted hydroxylapatite with a degree of substitution of $x = 1$ using other copper sources – Cu_2O, Cu, $(CuOH)_2CO_3$ – has been investigated. It is shown that any of the listed reagents, except metallic copper, can be used for this purpose, since in the latter case the formation of the unsubstituted hydroxyapatite and nanoscale copper particles is observed.

This research was carried out within a State Assignment to the Institute of Solid State Chemistry and Mechanochemistry SB RAS (project No. 121032500064-8).

STRUCTURAL FEATURES OF OXYAPATITE

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The apatite is a group of minerals with a general chemical formula $M_5(TO_4)_3X$ (Z = 2). One of the most widely known apatites is hydroxyapatite $Ca_5(PO_4)_3OH$. This mineral is a part of the human dental and bone tissues, and therefore is widely used in medicine for the reconstruction of bone defects. It is known that hydroxyapatite has a very low solubility in water [1], which slows down the process of its bioresorption. A review [1] reports that oxyapatite $Ca_5(PO_4)_3O$, which has the same biocompatibility as hydroxyapatite, has a significantly higher solubility. However, there is a limited information in the literature about its properties. It is reported that oxyapatite can be obtained by high-temperature treatment of hydroxyapatite, but the structural information of the material obtained by the different authors differs.

In this work, it was shown that oxyapatite can be obtained by heating of hydroxyapatite powder at 1000 ^{o}C under vacuum. FTIR and NMR spectroscopy prove the absence of the hydroxyl groups in the obtained apatite. In the IR spectrum, the presence of the new absorption bands of phosphate groups is observed, indicating a symmetry disorder. Density functional theory modeling confirmed lowering of symmetry for the oxyapatite structure. Modeling the IR spectrum of oxyapatite made it possible to identify the experimentally observed new absorption bands. According to the powder X-ray diffraction data, the presence of vacancy in a hydroxyl channel of the apatite structure lowers the symmetry to triclinic.

The study was supported by a grant Russian Science Foundation (RSF), No. 21-12-00251.

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MECHANOCHEMICAL PREPARATION OF BORON-CONTAINING COMPOUNDS WITH HAFNIUM

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The products of mechanochemical synthesis reactions in powder mixtures of hafnium (α-Hf) with carbon and with refractory boron-containing compounds (titanium diboride TiB_2, hexagonal boron nitride hBN, boron carbide B_4C) were studied using X-ray diffraction analysis, scanning electron microscopy and IR spectroscopy. It is established that under conditions of mechanical treatment in a high-energy planetary ball mill for 8 minutes, chemical interaction is realized in the equimolar composition of hafnium and carbon with the formation of nonstoichiometric hafnium carbide $HfC_{0.7}$ and the presence of traces of high-temperature modification of hafnium β-Hf. The particle size of mechanosynthesized carbide is less than 100 nm, and the crystallite size is about 17 nm. In the structures of boron-containing compounds during intensive mechanical activation for 2 minutes, changes occur associated with the appearance of boron carbide of non-stoichiometric composition $B_{6.5}C$ (for a mixture with B_4C), the appearance of pure boron (for a mixture with TiB_2) and activation of hexagonal boron nitride due to formation of intraplane defects in it (for a mixture in hBN). Mechanical activation of mixtures of hafnium and boron-containing compounds promotes the formation of dispersed composite aggregates with uniform grain-boundary distribution of hafnium and local formation of its compounds (borides and carbides), as well as oxides of hafnium and boron in mixtures of hafnium with BN and TiB_2. Presumably, powders with such a structure can provide reaction sintering to produce ultra-high-temperature ceramics of increased density.

The work was carried out within the framework of the state tasks of the ISSCM SB RAS (Project No. 121032500062-4) and state program of scientific research “Materials science, new materials and technologies” assignment 2.11 of JIME NASB.

SYNTHESIS OF HETEROPOLY ACIDS FROM ANTIMONY, MOLYBDENUM, AND VANADIUM OXIDES

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Heteropoly acids (HPA) are promising compounds for use in adsorption columns, filters, as they have a large surface area, channels of various sizes. Polyvalent ions are most often used as central atoms in HPA.

In this regard, the aim of the work was to select a procedure for the synthesis of heteropoly acids containing Sb^{+5}, Mo^{+6}, V^{+5} ions.

Sample synthesis: MoO_3, V_2O_5, Sb_2O_3 were subjected to mechanochemical activation in a porcelain mortar for 30 minutes. The molar ratios of the components $Sb^{+5} : Mo^{+6} : V^{+5} = 2/3 : 1/3 : 1/30$. Next, phosphoric acid (60%, 0.2 ml) was added to the resulting light orange powder. The sample was placed in water thermostated at 100 °C, after which the mother liquor was separated from the precipitate. The precipitate was dried and X-ray phase analysis was performed (DRON-3M, CuKα). To refine the HPA structure, the samples were dissolved in NaOH solution (0.1N). The structure fragments were constructed using the HyperChem program.

The phases $Mo_{0.32}SbO_{3.3}\cdot xH_2O$, $Sb_2O_5\cdot 4H_2O$, $MoO_3\cdot 2H_2O$, and H_2MoO_4 were indicated on the X-ray diffraction pattern of the sample (Fig. 1).

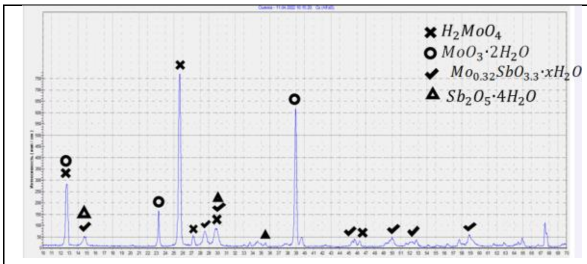

Fig. 1. Diffraction pattern of the synthesized HPA

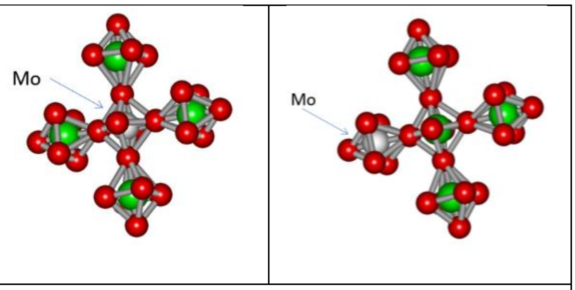

Fig. 2. Hypothetical structure of the samples HPA depending on the dissolution in NaOH

The synthesis was carried out in several parallels. The appearance of the diffractogram has not changed.

The structure of the HPA was refined according to the data of the dissolution of the samples in NaOH solution. Due to the difference in the amount of alkali for dissolving HPA, we assume that the central ion in HPA can be either Mo^{+6} or Sb^{+5} (Fig. 2).

MECHANOCHEMICAL SYNTHESIS AND REFINEMENT OF THE STRUCTURAL PARAMETERS OF SILVER FORMS OF POLYANTIMONIC ACID

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Inorganic ion exchange materials are highly thermally and atmospherically stable and have greater selectivity than organic ones. Such materials include polyantimonic acid (PSA) and its substituted forms. The main field of research in this paper are structural parameters of PSA silver forms. The synthesis was carried out by mechanochemical method: PSA and silver nitrate were put into a porcelain mortar and ground for 40 minutes. Then the sample dried for 1 hour at the temperature of 110°C. As a result, we have received fine powder of color ranging from white to bright yellow, depending on degree of substitution. Recovery processes with degrees of substitution x=0.2-1 (with step of 0.2) were chosen as study object. Structural studies were performed on a DRON-3M X-ray diffractometer. Using the Rietveld method in the PowderCell 2.4 program the occupancy of pyrochlore-type structures by ions, sp. gr. sym. Fd3m. was determined.

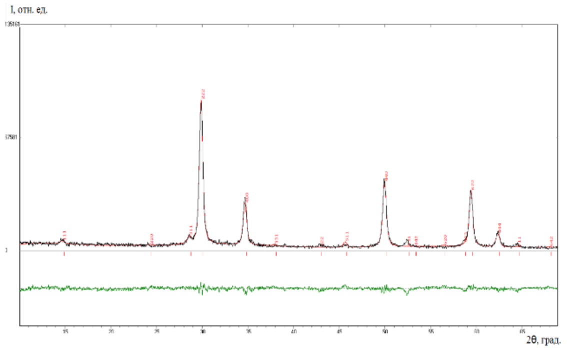

Fig. 1. Experimental and theoretical X-ray diffraction patterns of the sample $Ag_2Sb_2O_6 \cdot 2H_2O$.

The X-ray diffraction pattern (Fig. 1) shows a set of reflections corresponding to the structural type of pyrochlore. When protons are replaced by silver ions, a significant decrease in the relative intensity of the reflection is observed (I_{311}/I_{222}) (Fig. 2).

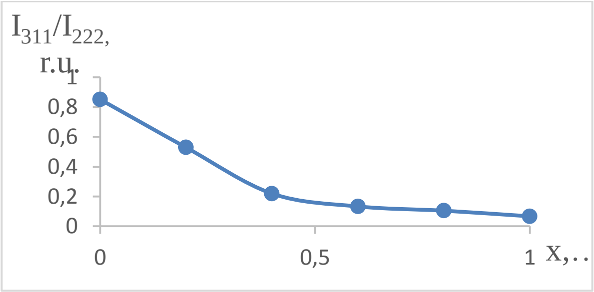

Fig. 2. Change in relative intensity of the PSA reflections.

SYNTHESIS AND STUDY OF THE PHASE COMPOSITION OF PEROVSKITE-LIKE OXIDES $La_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$

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Perovskite-like oxides of the composition $La_{1-y}Sr_yFe_{1-x}Co_xO_{3-\delta}$ (LSFC) with mixed ionic and electronic conductivity are of great interest for their application as electrode materials for solid oxide fuel cells/electrolyzers, etc. According to the literature data [1], varying the cations in A and B sublattices of these oxides can have a significant influence on the microstructure, the phase composition of the compounds, and as a consequence, improve the transport properties of the materials. The purpose of this work was to synthesize and study the phase composition of oxides based on $La_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$ ($0 \le x \le 0.2$).

Oxides of the composition $La_{0.5}Sr_{0.5}CoxFe_{1-x}O_{3-\delta}$ ($0 \le x \le 0.2$) were synthesized by the mechanical solid-state reaction method. According to the X-ray diffraction analysis (Figure 1), the synthesis by the ceramic method of oxides of the composition $La_{0.5}Sr_{0.5}CoxFe_{1-x}O_{3-\delta}$ ($0 \le x \le 0.2$) leads to the formation of non-stoichiometric perovskite with a rhombohedral R3c structure. Increasing the cobalt concentration in the LSFC structure leads to a cell parameter reduction in the unit.

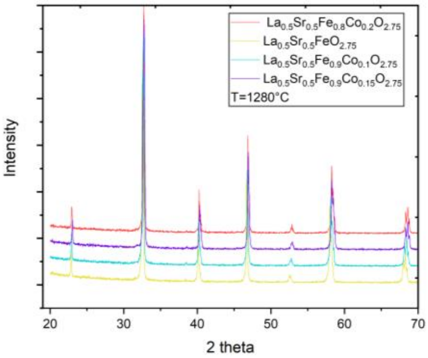

Fig. 1. X-ray diffraction of the oxides of the composition $La_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$ ($0 \le x \le 0.2$).

The work was performed within the framework of the state assignment of the Youth Laboratory "Materials and Technologies of Hydrogen Energy".

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OPTIMIZATION OF THE METHODOLOGY FOR MAKING SUSPENSIONS FOR THE CATHODIC AND ELECTROLYTE LAYER OF MT SOFCs

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Solid Oxide Fuel Cells (SOFCs) are environmentally friendly and efficient energy conversion devices operating at temperatures of 500 °C - 1000 °C. SOFCs designs are divided into planar, tubular, segmental, block, monolithic, etc. Planar SOFCs are considered to be more effective for high power generation. Nevertheless, there are areas in which tubular SOFCs design is preferable. For example, mobile and portable power generators for light vehicles, military and household appliances, various gadgets, for which the important parameter is the SOFCs launching rate, resistance to thermal cycling and electrical strain [1].

The aim of the work is to make cathode and electrolyte pastes for the formation of microtubular (MT) SOFCs by means of mechanical processing, as well as to determine the rheological properties of the obtained pastes.

Making oxide-based electrolyte and cathode pastes $Ce_{0.8}Sm_{0.2}O_{1.95}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) was held in the dissolver DISPERMAT LC-55 with a bead mill. Rheological properties of the obtained suspensions were determined by using a viscosimeter Brookfield DV3T-RV (Brookfield Engineering Labs Inc., USA).

The study was showed that the optimum viscosity of the solid phase for the electrolyte layer was 31 wt. %, for the cathode layer - 36 wt. %.

The work was performed within the framework of the state assignment of the Youth Laboratory "Materials and Technologies of Hydrogen Energy".

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MECHANOCHEMICAL SYNTHESIS OF $Ba_{0.5}Sr_{0.5}Co_{0.8-x}Fe_{0.2}Mo_xO_{3-z}$ PEROVSKITES AND STUDY OF OXYGEN TRANSPORT

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Nonstoichiometric oxides with mixed oxygen-electron conductivity are promising materials for oxygen-permeable membranes which can be used not only to obtain pure oxygen from the air and also for carrying out different petrochemistry processes and oxy-fuel combustion [1,2]. Membrane technologies are known to have economic and environmental advantages over traditional industrial processes. According to the literature data [2], the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) oxide, which has a cubic perovskite structure, has the highest oxygen fluxes and is best known in this field. However, the BSCF material is unstable at temperatures below 750°C. In addition, another problem that limits the practical application of this material is the degradation of BSCF oxide and oxygen fluxes in a CO_2-containing atmosphere.

The BSCFM oxides were synthesized by the mechanical solid-state reaction method. According to the data of XRD phase analysis, the BSCFMx (x=0; 2; 5% at) materials are single phased and have the structure of cubic perovskite $Pm\bar{3}m$. However, the XRD pattern of the BSCFMx sample (x = 10%) shows that, besides the basic reflections of the cubic perovskite (CP), additional reflections are observed that belong to the phase of the double perovskite (DP) $Ba/SrCoMoO_6$ with a tetragonal *I4/mmm* structure.

The oxygen permeability of BSCFM hollow fiber membranes was investigated. Partial substitution of cobalt cations in the BSCF structure by Mo^{6+} cations ($x \geq 0.1$) leads to increasing of oxygen fluxes compared to the undoped BSCF HF membrane. Mo-substituted HF BSCFMx membrane materials possess an improved performance in the presence of carbon dioxide during 180 h at T=650°C.

The work was performed within the framework of the state assignment of the Youth Laboratory "Materials and Technologies of Hydrogen Energy".

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EFFECT OF TUNGSTEN AND NIOBIUM DOPING ON LANTHANUM STRONTIUM FERRITE PEROVSKITE STRUCTURE

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Recently, high temperature solid oxide electrolysis cells (SOECs) have attracted great attention due to their efficiency for hydrogen production from renewable sources [1]. Moreover, it has been demonstrated that waste thermal energy from nuclear power plants and high temperature industrial processes can be used for steam electrolysis through a SOEC [2]. State-of-art SOEC electrode materials have some critical issues including stability at high temperatures and appropriate electronic and ionic conductivities [3]. Having mixed ionic and electronic conductivity (MIEC) and high redox stability, great variety of perovskites have been extensively studied as potential electrode materials.

In this work, two lanthanum strontium ferrite (LSF) perovskites, namely tungsten (W)- and niobium (Nb)-doped LSFs, were studied. Powders of $La_{1-y}Sr_yFe_{1-x}W_xO_{3-\delta}$ and $La_{1-y}Sr_yFe_{1-x}Nb_xO_{3-\delta}$ were synthesized via mechanochemical solid-state reaction route. Scanning electron microscopy was used to assess samples morphology. The effect of W and Nb doping on the LSF crystal structure was investigated using X-ray diffraction. The results indicated formation of rhombohedral structure ($R\bar{3}c$).

The work was performed within the framework of the state assignment of the Youth Laboratory "Materials and Technologies of Hydrogen Energy".

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STUDY OF THE FUNCTIONAL PROPERTIES OF $SrFe_{1-x}Mo_xO_{3-\delta}$ OXIDES PREPARED BY MECHANOCHEMICAL SYNTHESIS

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Mixed ionic electronic conducting oxides have attracted enhanced interest due to the possibility of their use as materials for catalytic membrane reactor for conversion of natural gas to synthesis gas, oxidative coupling of methane to value-added products [1, 2]. Among the oxides strontium ferrite is the promising materials for ceramic membranes. To improve the functional properties of membrane materials we previously proposed strategy based on doping of $ABO_{3-\delta}$ oxides with ferroactive highly charged cations B^{5+}/B^{6+}. The goal of the work is investigation the influence of Mo doping on oxygen permeability and phase stability of $SrFe_{1-x}Mo_xO_{3-\delta}$ oxides at low oxygen partial pressure and high temperatures.

The synthesis of the $SrFe_{1-x}MoxO_{3-\delta}$ ($0.02 \leq x \leq 0.25$) oxides was carried out by the mechanical solid-state reaction method from the corresponding oxides and metal carbonates. The detailed equilibrium phase diagrams “$3-\delta$ – $\lg(pO_2)$ - T” showed that partial isomorphous substitution of iron ions by molybdenum ($x \geq 0.02$) resulted in the broadening of the cubic perovskite phase stability region. The hollow fiber membranes were fabricated by phase inversion technique and their oxygen permeability was studied.

The work was performed within the framework of the state assignment of the Youth Laboratory "Materials and Technologies of Hydrogen Energy".

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DEVELOPMENT AND PRODUCTION OF AN ANODE MEMBRANE FOR SOFC

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Nowadays the transition to alternative energy sources is a global challenge due to the increase in CO_2 levels in the atmosphere and the greenhouse effect. The object of study in this work is anode micro tubular membranes for SOFC [1]. The purpose of the work is to select the composition of the composite powder, as well as to optimize the composition of the paste for the manufacture of MT membranes. A 60/40 NiO/YSZ composite powder was mixed using a bead mill with 2 mm ceramic balls. MT membranes were fabricated by the phase inversion method by extruding the paste through a spinneret. The composition of the paste includes a composite powder and an organic component. Studies have shown that the MT membrane has a porous finger-like structure, Figure 1. Pore formation occurs during polymerization while formation of MT membranes from a paste in distilled water. However, with high porosity, the percentage of shrinkage reaches 35% during sintering. When sintering, it is necessary to take into account the preservation of SOFC geometry, as well as the need to apply electrolyte and cathode layers. Thus, by reducing the proportions of the organic component in the paste, it is possible to control the porosity and hence the percentage of shrinkage. As a result of the work carried out to optimize the composition of the paste and composite powder, it was possible to achieve a shrinkage of the MT membrane of 25%, while maintaining high porosity and a special microstructure.

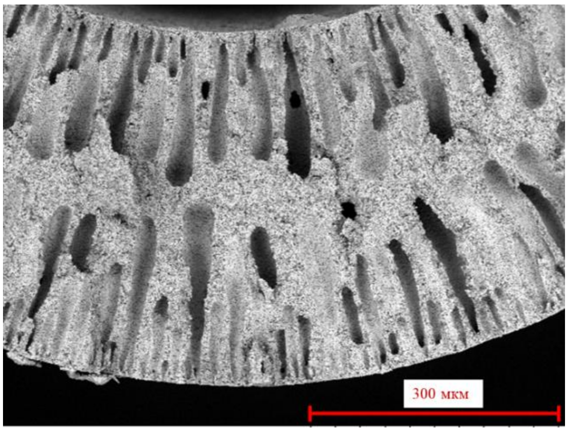

Fig. 1. MT membrane with a porous finger-like structure.

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INVESTIGATION OF OXYGEN EXCHANGE KINETICS BETWEEN COBALT-DOPED LANTHANUM NICKELATES AND THE GAS PHASE

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Complex oxides based on lanthanum nickelate $La_2NiO_{4+\delta}$ with mixed oxygen-ionic and electronic conductivity attract the attention of researchers as promising materials for the air electrode of electrochemical devices, such as solid oxide fuel cells and high-temperature solid oxide water vapor electrolyzers.

In this work, oxides based on cobalt-doped lanthanum nickelate $La_2Ni_{1-x}Co_xO_{4+\delta}$ ($x = 0 \div 0.2$) were synthesized by the mechanochemical method using an AGO-2 planetary ball mill. The solubility limit of cobalt in the nickel sublattice has been established. The kinetic parameters of the exchange of the synthesized oxide samples with the gas phase oxygen were first calculated using the oxygen partial pressure relaxation method [1]. The experimental data were processed using a kinetic model based on non-linear nonequilibrium thermodynamics and a macrokinetic tanks-in-series model. The temperature and oxygen partial pressure dependences of the surface exchange coefficient and the diffusion coefficient of oxides are obtained. The rate-determining stages of the exchange process are determined. The effect of doping with cobalt on the exchange and transport characteristics of oxides is analyzed.

The work was performed within the framework of the state assignment of the Youth Laboratory "Materials and Technologies of Hydrogen Energy".

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MECHANOCHEMICAL SYNTHESIS OF Nb- AND Ti- CONTAINING DRX OXIDES AS CATHODE MATERIALS FOR LITHIUM-ION BATTERIES

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Traditionally, the search for new cathode materials for lithium-ion batteries is carried out among compounds with a well-ordered crystal structure. In recent years, Li-excess cation-disordered oxides with the rock-salt structure (DRX) of the $Li_y(M_1M_2)_{2-y}O_2$ composition, where M_1 is an electrochemically active transition metal (TM) and M_2 is an electrochemically inactive d0 TM, are considered as promising cathode materials. These cathode materials have a high theoretical specific capacity (~300 mAh/g), which is achieved due to multielectronic processes involving two redox couples $TM^+/TM^{(n+1)+}$ and O^{2-}/O^-. Usually DRX oxides are obtained using the solid-state synthesis, including high-temperature treatment at > 900 °C. This method leads to the production of materials with micron-sized particles, which negatively affects the electrochemical properties of DRX oxide cathode materials. Therefore, the subsequent grinding is needed. On the other hand, it is known that the direct mechanochemical synthesis makes it possible to obtain materials directly in the nanoscale state.

In this work, the Nb- and Ti-containing DRX oxides were obtained by direct mechanochemical synthesis using various mixtures of the initial reagents: (1) Li_2O, Nb_2O_5, and Mn_2O_3, or (2) Li_3NbO_4 and $LiMnO_2$ for the synthesis of Nb-containing DRX oxides and (1) Li_2O, TiO_2, and Mn_2O_3 or (2) Li_2TiO_3 and $LiMnO_2$ for the synthesis of Ti-containing DRX oxides. Mechanical activation (MA) of mixtures of initial reagents was carried out using an AGO-2 planetary ball mill at 900 rpm.

According to the X-Ray powder diffraction, the as-prepared Nb- and Ti-containing DRX oxides are single-phase and crystallize in the disordered rock-salt structure with the *Fm-*3*m* space group. The formation of Ti-containing DRX oxides is observed after 30 minutes of MA, while the formation of Nb-containing DRX oxides needs 90 minutes of MA. On the other hand, the composition of the mixture of initial reagents does not significantly affect the duration of the process. This difference in the rate of synthesis of Nb- and Ti-containing DRX oxides is most likely due to the different hardness of the initial Nb- and Ti- containing precursors.

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SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF COMPOSITE ANODE MATERIALS BASED ON $TiNb_2O_7$

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Most commercial lithium-ion batteries (LIBs) use graphite as an anode material with a theoretical capacity of 372 mAh g^{-1}. When graphite is cycled below 1 V, it interacts with the electrolyte to form solid electrolyte interface (SEI), which leads to deterioration of the anode cycleability. Moreover, graphite anodes do not meet the requirements for high-power LIBs because of sluggish Li-ion diffusion and insufficient electrochemical kinetics. To avoid the formation of SEI and to improve kinetics, a lithium titanium spinel $Li_4Ti_5O_{12}$ has been developed. The drawback of $Li_4Ti_5O_{12}$ is its low theoretical specific capacity (175 mAh g^{-1}). In 2011, $TiNb_2O_7$ was proposed to replace $Li_4Ti_5O_{12}$. Its average lithium insertion voltage is about 1.64 V. The theoretical capacity of $TiNb_2O_7$ is 387.6 mAh g^{-1}. However, pure $TiNb_2O_7$ has poor electronic conductivity (10^{-9}–10^{-11} S cm^{-1}), which can be increased by obtaining this material as a composite with conductive materials. Moreover, the lithium diffusion coefficient of $TiNb_2O_7$ is also poor (10^{-15} cm^2 s^{-1}).

In this work, $TiNb_2O_7$ was prepared by the solid-state synthesis using TiO_2 and Nb_2O_5 with preliminary mechanical activation of the reagent mixture in AGO-2 for 5 min and subsequent heating at 1000°C for 4 h. To improve the power characteristics of $TiNb_2O_7$, two approaches were used: preparation of a composite with V_2O_3 to improve electronic conductivity and with $Li_3V_2(PO_4)_3$ to improve lithium ion conductivity. These composites were obtained by mechanical mixing of a pure $TiNb_2O_7$ with V_2O_5 or $Li_3V_2(PO_4)_3$ followed by annealing in an inert atmosphere to reduce V_2O_5 to V_2O_3 and prevent oxidation of $Li_3V_2(PO_4)_3$. The phase composition and crystal structure of the composites were studied by XRD with Rietveld refinement. Morphology of the sample was studied by scanning electron microscopy. According to the results of galvanostatic cycling in Li half-cells, the values of the specific charge capacity were equal to 290 mAh g^{-1} and 310 mAh g^{-1} for $TiNb_2O_7/V_2O_3$ and $TiNb_2O_7$/ $Li_3V_2(PO_4)_3$ composite anodes respectively, which are higher than that for pure $TiNb_2O_7$ (276 mAh g^{-1}). An additional peak was observed on the differential cycling curves related to the reduction/oxidation of vanadium compounds, which could affect the increased specific capacity values.

SUPERHARD VACUUM COATINGS

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To improve the quality of production processes and economic efficiency, it is necessary to use the full potential of wear-resistant superhard coatings. The most widely used coatings based on TiN, TiC and TiCN as a protective material for cutting tools, molds, parts and assemblies in mechanical engineering. The low chemical activity of these hard coatings protects the modified product from sticking of the treated metal and thereby reduces the adhesive wear of the tool.Studies conducted on the creation of multicomponent coatings have shown that compounds such as AlCrSiN and AlTiSiN can significantly increase the performance of vacuum coatings. The addition of Si and Al to TiN to form the AlTiSiN chemistry results in high performance coatings compared to TiN in terms of high temperature oxidation resistance, thermal stability and mechanical performance. According to preliminary studies, these multi-component nitride coatings have high wear resistance due to the formation of stable oxide layers on worn surfaces. It is also possible to introduce boron (B) into AlTiSiN, which leads to the formation of AlTiBN, and significantly increases wear resistance compared to TiAlN and TiBN. However, oxides formed in the area of tribocontact are not always effective in reducing friction and wear of materials, which depends on the morphology and process of chemical oxidation. The transformation of the morphology, microstructure, and mechanical properties of multicomponent coatings can be controlled by thermal oxidation or the introduction of carbon into three-component coatings. The micromorphology of multicomponent coatings was studied by optical microscopy, of the TiAlSi (N,C) system, formed on a base of various materials, depending on the conditions of preparation. These coatings are characterized by a smooth morphology, the coating is equidistant relative to the substrate surface. The formation of ultrasmall formations in the coating structure is observed, the concentration of which increases with increasing N,C concentration. The dependence of the coating morphology on the conditions for the formation of TiAlSi (N,C) layers is shown. The morphology of TiAlSi (N,C) coatings has been studied by atomic force microscopy; the formation of nanodispersed structures in the coating structure has been shown. The concentration of formations in the nanorange changes with variation in the bias voltage during the formation of a superhard coating.

DEVELOPMENT OF NiO/YSZ SUPPORTING ANODES AND YSZ SUPPORTING ELECTROLYTES FOR SOFC BY HYBRID 3D-PRINTING

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At the present time, solid oxide fuel cell (SOFC) is one of the most common converter of hydrogen combustion energy into electrical energy. Solid oxide fuel cells have a number of undisputed advantages, such as high efficiency of fuel conversion, environmentally friendly waste during combustion. Despite all the above advantages of SOFCs, they are practically not manufactured on an industrial scale due to the difficulty in scaling up production [1].

In recent years, there has been a significant progress in 3D printing technologies for the manufacture of both individual elements of solid oxide fuel cells and a complete SOFCs stacks [2]. In this work, the printing compositions (pastes) based on nickel oxide and yttrium-stabilized zirconium oxide obtained in a laboratory submerged ball mill for hybrid inkjet 3D printing with laser treatment were developed and investigated. The rheological parameters of the pastes were studied depending on the nature of the dispersed filler. Experiments were carried out for printing two-dimensional and three-dimensional objects - an electrolyte and an anode - on a 3D printer using selected printing compositions. The influence of laser processing and printing regimes was studied; the printing regimes on the morphological features of the supporting anode and supporting electrolyte based on nickel oxide and zirconium oxide were studied. Experimental samples of a given shape and size were obtained.

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MECHANOCHEMICAL SYNTHESIS OF Li-ION CONDUCTING MATERIALS WITH GARNET STUCTURE

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At present, $Li_7La_3Zr_2O_{12}$ (LLZO) with a garnet structure are of great interest as solid state lithium conductors due to their high ionic conductivity ($>10^{-4}$ S/cm) and resistance to lithium metal. LLZO has two crystal modifications: high-temperature cubic with a conductivity of 10^{-4} S/cm and more and low-temperature tetragonal (10^{-7}-10^{-6} S/cm). To stabilize the cubic structure at room temperature, various doping additives are used, such as Al, Nb, Ta, Rb, Ga, Mg, Sr, Ce, and others.

Synthesis of LLZO consists in high-temperature treatment of a mixture of initial reagents. In this case, various methods of homogenization and grinding of reagents are used (modified Pechini method, sol-gel method, mechanical mixing of substances). Depending on the chosen method, the synthesis temperature varies from 900 °C to 1200 °C, in connection with which an excess amount of lithium (10-15% by weight) is introduced into the initial mixture of reagents.

In the proposed work, we used the method of mechanical mixing of the initial reagents in a liquid medium of ethanol using zirconium ceramic balls as grinding bodies in a vertical submersible mill. At the same time, during processing, grinding and homogenization of the reagents occur simultaneously. This method is easy to perform, scalable, allows easy regeneration of consumables (alcohol), and there is no need to use large amounts of auxiliary components. Aluminum was used as a doping element to obtain a product of composition $Li_{6.28}La_3Zr_2Al_{0.24}O_{12}$ with a cubic structure. For commercial products of this composition, a temperature of 1000 °C is used. The method used provided finer grinding and homogenization of the reaction mixture, which led to a decrease in the synthesis temperature to 900 °C. This made it possible to reduce the excess amount of lithium in the mixture to 6% by weight to compensate for lithium losses due to evaporation.

DRY PLANT EXTRACTS AS A BASIS FOR BIOLOGICALLY ACTIVE NUTRITIONS

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The possibilities of using dry plant extracts to obtain solid forms of biologically active additives are described. Betulin and betulonic acid, were used as biologically active components. The formation of supramolecular systems for the "delivery" of biology active molecules is provided by glycyrrhizic acid micelles [1]. They formed after dissolution of mechanochemically obtained solid dispersions which including the above components with a dry extract of licorice roots containing up to 20% by weight of glycyrrhizic acid. The formation of its micelles upon dissolution of the extracts is shown by gel-penetrating chromatography.

In all cases, a significant increase in the solubility of active substances, transmembrane permeability and pharmacological activity was achieved. The use of dry extracts has an advantage over pharmacopoeia components based on their availability and reduced cost.

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[1] A.V. Dushkin, E.S. Meteleva, T.G. Tolstikova, et al. Chemistry for Sustainable Development. 27 (2019) 233-244.

PREPARATION AND PHYSICO-CHEMICAL INVESTIGATION OF VALSARTAN SELF-MICELL SOLID DISPERSION WITH DISSODIUM GLICYRRIZIN

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Valsartan is a BCS class II drug (structure is shown in Figure 1).

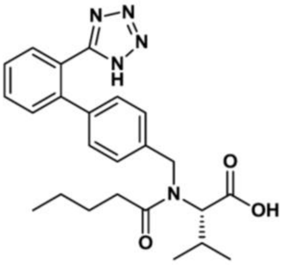

Fig. 1. Structure of valsartan.

It is an efficacious blood pressure-lowering active pharmaceutical ingredient (API), but its absolute bioavailability is only 25%, following oral administration on account of its poor aqueous solubility. To improve the solubility of valsartan, an amorphous solid dispersion (SD) of Valsartan (Val) with disodium glycyrrhizin (Na2GA) was prepared by mechanochemical method. The physical properties of Val SD in solid state were characterized by differential scanning calorimetry, X-ray diffraction studies, and scanning electron microscope. The characteristics of the sample solutions were analyzed by reverse phase HPLC, 1H NMR spectroscopy. The parallel artificial membrane permeability assay (PAMPA) was used for predicting passive intestinal absorption. The Val solubility from obtained SD is more than 100 folds higher than Val API. But VAL permeation throws artificial membrane from solutions of SD is lower than from solution of Val API. The only reasonable explanation of the discovered contradiction is that increasing of solubility reaches by ionization and salt formation. So, charged forms of Val molecules cannot be accepted by hydrophobic membrane. This explanation is confirmed by PAMPA experiments at different pH values.

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MECHANOCHEMICAL APPROACH TO THE PREPARATION OF COMPLEX ANTIHELMINTHIC DRUGS

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Currently, the problem of helminthoses remains very relevant. Most of the widely used drugs for control and treatment of helminthosis are poorly soluble in water and, as a result, have low efficiency. Mechanochemical methods for increasing their solubility and combining several substances to form supramolecular systems that include molecules of these anthelminthic substances and polymers are promising for their improvement.

In this work, we studied the possibility of preparation of complex drugs based on such well-known anthelminthic substances as fenbendazole (FBZ), fenasal (FNS) and praziquantel (PZQ) with polyvinylpyrrolidone (PVP) and licorice extract (EL).

Table. Increasing the solubility of anthelminthic substances in complex drugs.

No	Composition, conditions of mechanochemical method	Increase in solubility	
		FBZ	FNS
1	FBZ:FNS:PVP (2:30:298), LE-101, 5 h	6.4	27.2
2	FBZ:FNS:PVP (3:30:297), VM, 24 h	52.0	74.6
3	FBZ:FNS:EL (2:30:298), LE-101, 5 h	107.0	1.1
4	FBZ:FNS:EL (3:30:297), VM, 24 h	175.0	83.3
5	FBZ:PZQ:PVP (2:1:27), LE-101, 5h	Increase in solubility	
		FBZ	PZQ
		0.7	2.5
6	FBZ:PZQ:PVP (2:1:27), VM, 12 h	17.0	2.0
7	FBZ:PZQ:EL (2:1:27), LE-101, 2 h	7.9	4.3
8	FBZ:PZQ:EL (2:1:27), VM, 4 h	8.0	2.0

The resulting drugs in the form of solid dispersions had increased solubility that suggested a high anthelminthic activity. Since solid dispersions based on these substances were effective in experimental trichinellosis of white mice (85%).

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MECHANOCHEMICAL SYNTHESIS OF SOLID COMPOSITIONS OF ALBENDAZOLE FOR IMPROVEMENT OF THEIR ANTIHELMINTHIASES ACTION

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All over the world and in particular in the Russian Federation, agricultural’s animal helminthiases are widespread, which often lead to the death of animals and economy damage. For the treatment of animals, the drug albendazole (ABZ) is used, which has a wide spectrum of action. Along with this, albendazole has a number of disadvantages, namely, poor solubility, low permeability and bioavailability and embiotropic activity. In this regard, the purpose of this work was to increase the effectiveness of albendazole and reduce the action therapeutic dose. To do this, we used a mechanochemical technology to obtain solid disepersions of ABZ with especially additive component, which forms supramolecular complexes after dissolition.

In this work, dry extract produced from roots of *Glycyrrhiza uralensi* growing in the Siberian region was used as an adjuvant substance, which contains glycyrrhizic acid as far as poly- and oligo-saccharides as the main components. The noted components provide improvement of solubility and trans-membrane transfer by inclusion of ABZ molecules in micelles formed by glycyrrhizic acid and in complexes with polysaccharides.

Composition of ABZ/licorice extract were obtained by mechanochemical way with different weight ratios. The compositions were investigated in solid state and in solutions using a variety of physicochemical methods. It was shown that solubility increases for many folds times in all compositions. The PAMPA assay method (measurement in vitro permeability throw artificial membranes) was used to evaluate the intestinal permeability. It is shown that in all cases, the solutions from obtained solid dispersion have very significant advantages in the comparison with officinal ABZ.

Optimal formulations were tested for anthelmintic activity on laboratory animal models and in field conditions on sheep. The results are presented in the article [1].

The research was carried out with the support of the Ministry of Science and Education of the Russian Federation of the project No. 121032500061-7.

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CO-PROCESSING OF COAL AND PINE IN ROLLER MILL: COMPOSITE FORMATION

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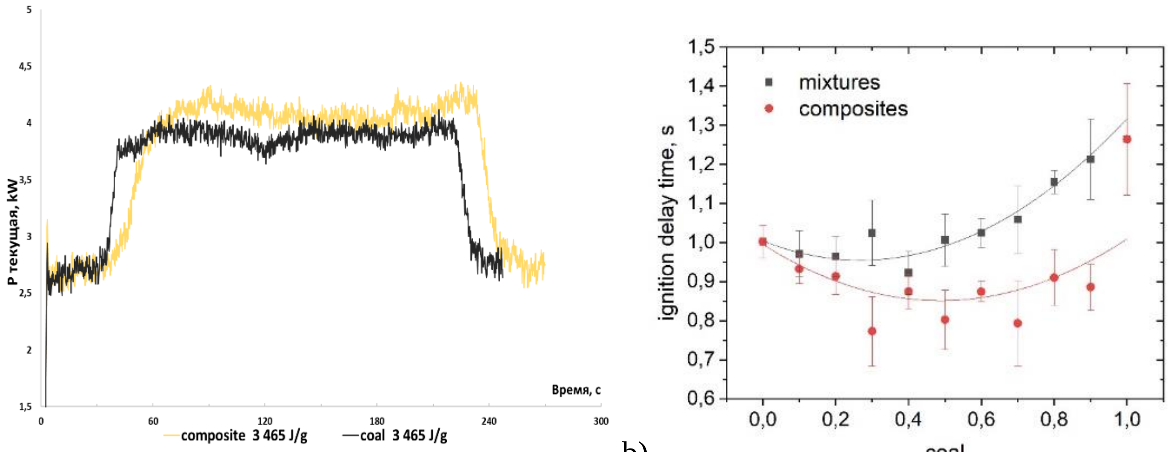
It is known that the simple addition of wood powder leads to acceleration of coal powder ignition in comparison with the pure coal case. The aim of the work was to determine the optimal parameters for the joint mechanical processing of coal and pine powder, leading of composites formation [1]. Firstly, we show that the current power consumption has no differences between joint and separate milling cases (Fig. 1a).



a) b)

Fig. 1. a) Energy consumption during the joint and separate processing of coal and pine sawdust. b) Dependence of the ignition delay time of composites and coal-sawdust mixtures on the coal content.

Next, it was shown that obtained material is composite – coal-covered pine particles. As co-combustion of coal with sawdust has a synergistic effect [2], the optimal ratio of pine sawdust and coal was found, equal to 30% and 70%, respectively. Especially this synergy depends on the "geometry" of the mixture - a simple mixture or obtained composite material (Fig. 1b).

This work was supported by RF Ministry of Science and Education, project No. 121032500067-9.

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ISOLATION AND CHARACTERIZATION OF CHITIN FROM HONEYBEE CORPSES AND SQUID PENS

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Chitin is the most abundant derivative of cellulose consisting of 1,4-β-N-acetyl-2-aminodeoxyglucose units [1]. Chitin is of scientific interest due to a huge number of applications. Chitin is used as a carrier material for drugs, a substrate for cell cultivation for the production of artificial skin, food additives, a reinforcing component of paper, etc. [2]. In nature there are three polymorphic modifications of chitin: α-, β- and γ-chitin. In industry, α-chitin is isolated from crustacean shells. Insects can be an alternative source of α-chitin, e.g. bee corpses. Molluscs are often used as a natural source for β-chitin extraction.

The work is aimed at obtaining and characterization of α- and β-chitin from animal raw materials by the example of bee podomor and squid pens.

Methods for isolation of α- and β- modifications of chitin from bee corpses and squid pens, respectively, were perfected in this work. The obtained samples were characterized by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). Crystallinity indices were determined according to the method proposed by Focher et al. [3]. Using the XRD method, it was found that the crystallinity index for α-chitin increased during chitin separation from 78 to 93% and for β-chitin from 48 to 62%. According to SEM results, it was shown that chitin particles had a homogeneous fibrous structure.

As a result, α-chitin from bee corpses and β-chitin from squid pens were obtained, and polymorphs were characterized by XRD and SEM methods. An increase in the crystallinity index of chitins during chitin isolation was shown. The shape of α- and β- chitin particles was also determined.

The study was supported by the state assignment to the Institute of Solid State Chemistry and Mechanochemistry SB RAS (project no. 121032500067-9).

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DEVELOPMENT THE TECHNOLOGY OF GLYCOSYLATION OF QUERCETIN IN *FILIPENDULA ULMARIA* MAXIM.

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Flavonoids as products of species-specific plant metabolism are of interest as a basis for the development of new medicines. Among all flavonoids, flavonoids of the quercetin group and, above all, rutin play a significant role. Rutin has a capillary-strengthening effect, which is important for stroke prevention. One of the perspective sources of rutin is meadowsweet (*Filipendula Ulmaria* Maxim.) with the prevalence of rutin aglycon - quercetin. One way to increase the extractability is to use mechanoactivation and conduct a glycosylation reaction.

The aim of this work was to investigate the effect of solid-phase mechanochemical pretreatment on the composition and flavonoid content of model flavonoid solutions and extracts of meadowsweet.

As a result of our research work, we found that the glycosylation of quercetin is only observed when magnesium oxide is used as a catalyst. Thermal treatment increases the yield of the glycosylation reaction, while intensive mechanical treatment reduces the yield. The heat treatment in an inert medium at 150 °C for 2.5 minutes using magnesium oxide leads to a quercetin glycosylation yield of 6.38%, which is 10 times higher than the previously known methods.

The use of the quercetin glycosylation technique with real plant material results in the glycosylation of quercetin in a yield of 1.2%, which is almost 2.35 times higher than the yield of rutin from meadowsweet under normal extraction conditions. Thermal treatment in an inert medium has no effect on the increase in the yield of the glycosylation reaction.

The quercetin glycosylation product was studied in vitro on cell cultures. It was shown to stimulate the growth of interferon-γ, interleukin-1-β, tumor necrosis factor-α at 1 μmol/l and inhibit the growth of granulocyte-macrophage colony-stimulating factor and interleukin-12-α at 10 μmol/l, indicating an anti-inflammatory effect and an immune-stimulating effect.

Thus, this technique of glycosylation of quercetin can be applied to the creation and production of medicines and food supplements containing medicinal plant raw materials.

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PECULIARITIES OF SORPTION OF HEAVY METALS BY MECHANOCHEMICALLY MODIFIED NATURAL POLYPHENOLS

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Polyphenolic compounds of natural origin are widely used to increase the productivity and environmental cleanliness of modern agriculture and in environmental management. It is assumed that the products obtained by mechanochemical technology will have a certain degree of oxidation and controlled redox and adsorption characteristics, which is in demand in the production of products for preventive and functional nutrition, for agricultural and environmental purposes.

Humic acids and melanins are polymeric polyphenols with amphiphilic properties containing various functional groups. In particular, the ion-exchange properties of these polyphenols are provided by a high content of carboxyl and phenolic groups [1]. Some examples of success mechanochemical modification of the structure and properties of humic acids in brown coals are known [2].

The aim of this work is to study the effect of oxidative mechanochemical treatment of humic acids and melanins on the ability to remove heavy metal ions from water.

Mechanochemical treatment of humic acids and melanins with and without reagents was carried out in mechanochemical activators of planetary type AGO-2, with steel drums and balls. The IR spectra of the obtained samples were studied, indicating the disappearance of the band at 1710 cm $^{-1}$ related to carboxyl groups for the samples obtained by treatment with sodium percarbonate. The potentiometric back titration of polyphenols was carried out, the content of three types of functional groups with acidic properties was calculated.

The sorption of heavy metals (Zn^{2+}, Cd^{2+}, Cu^{2+}) by modified polyphenols was studied. All polyphenols show high sensitivity to heavy metals from water. Thus, the sorption values for the original, mechanochemically and chemically activated humic acids density 39.7±0.1; 30.7±0.1; 28.1±0.1 mg(zinc)/g(sorbent), respectively.

This study was supported by the Russian Science Foundation (project no. 21-13-00046).

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MECHANISM STUDY OF BETULIN - CARBOXYLIC ACIDS CO-CRYSTALS FORMATION BY MECHANOCHEMICAL METHOD

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Betulin, lup-20(29)-ene-3β,28-diol, extracted from birch bark, exhibits various types of pharmacological activity, including antiviral, antibacterial, anti-inflammatory, anti-HIV, or anti-cancer effects [1]. However, betulin is slightly soluble in water, and this substantially limits its bioavailability.

In our previous works [2], some new crystalline forms of betulin in the mixtures of betulin with dicarboxylic acids (adipic, suberic, or terephthalic) were obtained with the help of the liquid assisted grinding (LAG) method. These forms were attributed to cocrystals of betulin. They revealed improved solubility in comparison with initial betulin.

It is well known that under the conditions of LAG synthesis, shear deformations and a local increase in temperature occur. To elucidate the mechanism of co-crystal formation, namely: the role of heating during mechanical treatment, the mixture of reagents was heated and the obtained products were compared. The experiments on betulin heating in the presence of dicarboxylic acids, adipic or suberic, revealed that the morphological changes can serve as a test for cocrystal formation. The XRPD patterns of the heated betulin – adipic acid physical mixture were similar to those of the mixtures ground in the presence of a liquid with the formation of a cocrystal.

The research was carried out within the state assignment to ISSCM SB RAS (project No. 121032500064-8) and to ICCT SB RAS (project No. 121031500180-8).

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EFFECT OF MECHANICAL ACTIVATION IN THE PRESENCE OF SOLVENTS AND CO-FORMERS ON THE STRUCTURE OF BETULIN DIACETATE

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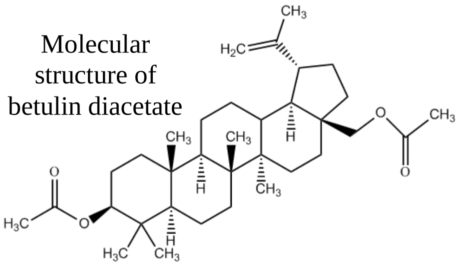

Molecular structure of betulin diacetate

Betulin isolated from birch bark, like its derivatives, has a wide spectrum of pharmacological activity. However, their low water solubility hinders their bioavailability. We have previously shown that, upon mechanical activation, betulin forms cocrystals with dicarboxylic acids [1, 2], which have increased solubility in aqueous solutions. It is of interest to find out whether betulin derivatives, in particular, betulin diacetate, will form cocrystals. In this work, experiments were carried out on the mechanical treatment of betulin diacetate (BDA) with potential co-formers - both dicarboxylic acids with different hydrocarbon chain lengths (adipic, sebacic) and nitrogenous bases (guanine, thymidine). Mechanical treatment was carried out in a Spex mill using treatment time 15 min, ball weight 40 g, sample weight 0.5 g. A small amount of a solvent, ethanol or dioxane, was added to the processed mixture to speed up the process (the solvent-drop grinding method). The results showed that while mechanical activation of BDA without solvent results in an amorphous product, in the presence of small amounts of solvents, a crystalline form of the substance is formed as a result of its crystallization in a mill in the presence of a solvent. Taking into account that the amount of solvent used is obviously insufficient for the dissolution and crystallization of the entire substance, an important role is apparently played by the appearance of nuclei of a crystal phase, which causes its spontaneous growth. BDA, in contrast to betulin, does not form cocrystals with dicarboxylic acids, which may be due to the low activity of BDA C=O groups for the formation of hydrogen bonds or their shielding in the BDA structure.

The research was carried out within the state assignment to ISSCM SB RAS (project No. 121032500064-8) and to ICCT SB RAS (project No. 121031500180-8).

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SYNTHESIS OF DIACYLES OF BETULIN FROM ACTIVATED BIRCH BARK

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In recent years, the interest of scientists from different countries in triterpenoids of the lupan series, in particular, in betulin and its derivatives, has increased in connection with their proven antiviral and antitumor activity. The availability of raw materials (birch bark) and high biological activity put betulin in a number of valuable natural sources for the synthesis of new dietary supplements and medicinal substances [1].

Well-known methods for producing betulin diacyles are multistage, require the use of expensive and toxic chemicals: pyridine, benzene, carboxylic acid anhydrides, and are based on the acylation reactions of betulin isolated from birch bark. To intensify the processing of plant raw materials, mechanical activation methods are successfully used to facilitate extraction and increase the yield of products.

The purpose of this work was to study the effect of the degree of birch bark grinding, as well as the treatment of birch bark with superheated water vapor, followed by a sharp pressure release, on the yield of betulin diacyles and other products.

A one-stage method for obtaining betulin diacyles directly from birch bark without a separate stage of betulin isolation has been developed at the Institute of Chemistry and Chemical Technology SB RAS. Preliminary activation of the original birch bark leads to loosening of its structure and hydrolysis of weak bonds, which contributes to a more efficient delivery of reagents and a reduction in the duration of acylation processes, as well as an increase in the yield of target products.

It has been shown that the preliminary activation of birch bark with superheated water vapor and the subsequent abrupt release of pressure make it possible to reduce the duration of acylation and obtain products with a high content of betulin diacetate and dipropionate.

The research was carried out within the state assignment to ICCT SB RAS (project No. 121031500180-8).

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BENDING AND BRITTLE ORGANIC CRYSTALS OF PYRAZINAMIDE: A COMPUTATIONAL APPROACH

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Mechanical properties of initial reagents are highly important for mechanochemical processes and technologies, taking into account not only reactions, but also grinding. For a long time, it was supposed that organic crystals were generally brittle, until the first reports of crystals capable of significant plastic and elastic deformations appeared. One of the examples of unusual mechanical behavior, the ability of crystals to plastically bend in noticeable extent, is quite rare (no more than 100 examples per ~3 million organic structures in the database). At the same time, the qualitative model currently prevailing in the field[1] is not rigorous enough: among organic crystals, layered structures are common, as is the anisotropy of the forces of intermolecular interactions. Moreover, some bending crystals do not fully fit into this model.[2] Thus, a quantitative approach is needed to predict such crystals.

In this study, we make an attempt to determine those structural descriptors that make it possible to predict the bending of organic crystals. To eliminate the influence of the composition we chose as an object of study a system of polymorphic modifications of pyrazinamide, among which there is a bending (alpha) and non-bending (delta) form. It was shown that the energy of sliding layers in alpha and delta forms differ substantially as well as macroscopic mechanical properties using Molecular Mechanics (MM) and periodic DFT methods. Provided research gives and insight on possible quantitative indicators for predicting plasticity of molecular crystals.

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MM AND DFT STUDY OF ELASTIC, BRITTLE AND PLASTIC 4-BROMPHENYL 4-BROMBENZOATE CRYSTALS

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The plasticity of organic crystals is a relatively new phenomenon that has attracted the attention of many research groups [1-3], albeit it is not fully understood. Mechanical properties of organic crystals, used for further mechanical treatment may be crucial for the production technology of final product, e.g., tableting of pharmaceuticals. Nevertheless, the main theoretical explanation in literature, proposed by Reddy et al., is only illustrative and does not contain specific quantitative criteria [1].

Computational methods may answer multiple questions of this phenomena, including exact estimation of intermolecular interactions in ideal crystal structures. The main goal of this work was to consider possible calculation methods for studying the plasticity of organic crystals, and then, to find parameters that could be decisive for the macroscopic properties of a substance.

4-bromophenyl 4-bromobenzoate contains three polymorphs with known layered crystal structures studied experimentally [4] and theoretically [5] and was chosen for this work. Our study results show different stability of three forms, coinciding well with literature data. Various theoretical methods for these structures have been processed: classical crystallographic analysis, BFDH morphology prediction model, calculation of intermolecular energies using the MM and DFT methods. Our preliminary study shows strong correlation between the energy of the inter -layer energy and mechanical properties.

This work was supported by Russian Science Foundation, grant number 21-73-00094 (https://rscf.ru/en/project/21-73-00094/).

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UHMWPE CRYSTALLINITY AND CONCENTRATION INFLUENCE ON THE PROPERTIES OF THE MECHANOSYNTHESIZED UHMWPE/OXIDE COMPOSITES

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The development of new light composite materials with possibility of properties forecasting and improvements in performance characteristics are impossible without accounting of formation processes where polymer crystalline structure, particles-to-polymer interphase and surfaces behavior plays a significant role in charge distribution. Fine particles of iron oxides have been applied for modification of ultra-high molecular weight polyethylene (UHMWPE) to synthesize powdered composites for subsequent hot pressing. A combination of polymer, particles and interphases possesses proper electrical and magnetic losses result in microwave absorption properties. We investigate composite materials synthesized by hot pressing from UHMWPE/oxide mechanoprecursors with different dispersion and mutual concentration. Dielectric properties were analyzed by Dielectric Spectroscopy testing frequency dependence of the permittivity, dielectric losses, and conductivity. The interdependence of structure morphology and dielectric properties have been analyzed by means of Scanning Electron Microscopy, X-ray Diffraction, IR-spectroscopy, Mössbauer Spectroscopy and Differential Scanning Calorimetry. The versatility of the composite was such that its own dielectrical properties can fluctuate according to the filler ratio and particles sizes within polymer. By varying the filler volume percentage, it is possible to minimize the unwanted contribution to the dielectric constant and dielectric losses under designing the magnetically active light composite.

THE EFFECT OF THE PARTICLE SIZE OF MgFeGa-LAYERED TRIPLE HYDROXIDES ON THE FIRE-RESISTANT AND MECHANICAL PROPERTIES OF POLYURETHANE

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Layered hydroxides are considered as a new type of environmentally friendly flame retardants for polymers as a result of high fire resistance and smoke suppression. In addition to the behavior of flame retardants during thermal decomposition, the size of its particles also plays an important role affecting the fire resistance of materials.

In this paper, the effect of the particle size of MgFeGa-layered triple hydroxides (MFG-LTH) on the fire-resistant mechanical properties of injection-molded polyurethane is investigated.

According to X-ray diffraction studies, the synthesized MFG-LTH sample corresponds to the structure of layered hydroxides. All the main peaks of the hydrotalcite-like structure are present on the diffractogram.

Thermogravimetric analysis showed that as a result of heating up to 800 ^{o}C, three stages of mass loss are observed for LTH: up to 100 ^{o}C, 100 to 260 ^{o}C and 260 to 800 ^{o}C.

Composites were obtained by introducing MFG-LTH in an amount of 5 wt. % in-situ into a polyurethane prepolymer during synthesis, when the initial components were in a liquid state, followed by curing in an open form at 100 ^{o}C.

The fire resistance of polyurethane composites was investigated in accordance with GOST 27484. It is determined that the fire resistance of composites based on MFG-LTH with a larger size is higher than with a smaller one. The use of MFG-LTH flame retardants with a smaller particle size leads to a decrease in the mechanical characteristics of composites.

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SYNTHESIS OF BIOPOLYMER-BASED HYBRID INORGANO-ORGANIC NANOCOMPOSITES

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Nowadays, the synthesis of metalloid-derived polysaccharide hybrid nanocomposites represent a challenging and hot direction in the design of both pharmaceutical substances and functional materials, which can find a wide application in various fields of science engineering.

Unfortunately, the boundary between the minimum allowable levels of intake of selenium or tellurium to the organism and toxic effects of these elements is very narrow. To address this issue, nano-sized metalloids are introduced into the organism, since, unlike elemental selenium or tellurium, nanoparticles of these biogenic elements exhibit higher biological activity and lower toxicity. In terms of "green" chemistry paradigm, the most promising method for the synthesis of such nanoparticles is assumed to be the design of their compositions in a stabilizing matrix. At the same time, the matrix itself should possess a wide range of functional properties. Such properties are inherent, for example, in the natural polysaccharide arabinogalactan (AG), extracted from Siberian larch wood. AG combines water solubility with such unique biological features as immunomodulatory and membranotropic activity that favorably differ this polysaccharide from other natural macromolecules.

In the present work, hybrid nanocomposites of selenium or tellurium have been synthesized by mechanical activation of metallic selenium and tellurium particles into AG polymer matrix. The obtained nano-sized composites were characterized by XRD, HR TEM, and UV spectroscopy. Antimicrobial activity of the composites with respect to microorganisms of various taxonomic groups was determined.

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