INSTITUTE OF SOLID STATE CHEMISTRY AND MECHANOCHEMISTRY SB RAS

NOVOSIBIRSK STATE UNIVERSITY

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## V International Conference
## «Fundamental Bases of Mechanochemical Technologies»

## FBMT- 2018

# BOOK of ABSTRACTS

Novosibirsk

2018

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# PREFACE

Welcome to the FBMT 2018! The V International Conference “Fundamental Bases of Mechanochemical Technologies” (FBMT 2018) will be held on June 25-28, 2018 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 and Novosibirsk State University.

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 joint 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 Novosibirsk State University in the organization of this Conference guarantees active participation of young scientists in the Conference. The Conference has attracted a total of 230 contributions; 110 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 2018:

- Novosibirsk State University,
- Federal Agency for Scientific Organizations,
- Russian Foundation for Basic Research,
- NOVIC Co.,
- ABEX Co.

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 2018

## SCOPE OF THE CONFERENCE

The V International Conference “**Fundamental Bases of Mechanochemical Technologies”** is devoted to all aspects of theory, methods and applications of mechanochemistry. The Conference will provide a forum for chemists, physicists, materials scientists, engineers and industry representatives to discuss the most recent achievements and current challenges of the fascinating field of mechanochemistry. The Conference will offer a lot of opportunities for exchanging ideas and finding new research partners. The contributions are expected to be focused on traditional and novel subjects of mechanochemistry including but not limited to:

- Theoretical aspects of mechanical activation. Mechanochemical reactions: kinetics and mechanisms.
- Mechanochemical synthesis. Mechanical alloying.
- Mechanochemistry of organic systems and plant raw materials.
- Mechanochemistry for the design of new materials including materials for energetics and additive technologies.
- New mechanochemical technologies.

## BACKGROUND OF THE CONFERENCE

FBMT-2018 is the latest in the series of FBMT conferences previously held in Novosibirsk, Russia in 2001, 2004, 2009, 2013. These conferences have promoted dissemination of research results in the field of mechanochemistry and facilitated interactions between scientists and industry.

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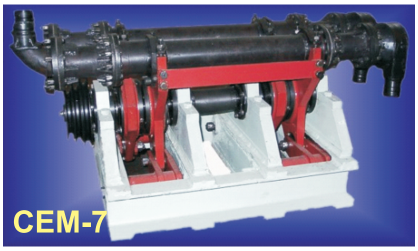
НОВИЦ

# MILLS AND MECHANOCHEMICAL ACTIVATORS

**Mills of «CEM», «AGO», «APF» types have been designed at the Institute of Solid State Chemistry and Mechanochemistry SB RAS and patented.**

## Mills of «CEM» type are successfully used:

- to grind and activate brittle substances and natural minerals with hardness up to 8-9 units to prepare construction materials;
- in technological lines manufacturing various types of ceramics, pigments, fertilizers, medicines;
- in the production of new materials as chemical reactors.



| TECHNICAL CHARACTERISTICS | CEM-7 | CEM-20 |
|---|---|---|
| Operational mode | Continuous or discrete | |
| Power of the electric motor, kW | 5 | 18 |
| Productivity in continuous mode ( e.g. for sand), kg/hour | 20-50 | 850-1200 |
| The maximum initial size of material particles, mm | 3 | 5 |
| Size of particles after milling, μm | 5-20 | 10-60 |
| Overall dimensions (length/ width/ height), mm: | 700/540/420 | 1910/1225/870 |
| Weight, kg | 235 | 1300 |

## PLANETARY AGO MILLS - ONE OF THE MOST POWERFUL IN THE CLASS

Full milling time (up to 1-5 microns) - from 30 sec. (!) up to 5 minutes. The important advantage of these mills is the very intensive water cooling that prevents the milling material from overheating typical for conventional planetary mills.

Can be delivered with a touch-screen control panel.

## Planetary mills are successfully used:

- for thin and super-thin crushing of inorganic hard and super-hard materials;
- for mechanochemical activation of inorganic materials;
- for extraction of poorly soluble components in the environment of a solvent;
- for synthesis of new materials, composites, catalysts.

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КОМПАНИЯ АБЕКС
БИОКОМПОЗИТ ™

ABEX is a Russian company, founded in 2012, for the introduction of technologies based on mechanochemical activation of plant raw materials in the production of biologically active additives.

Within a short period of time, the company managed to launch a line of parafarmaceuticals "Biocomposite", created on the basis of a unique mechanochemical technology and having no analogues on the pharmaceutical market. The highest bioavailability and effectiveness of drugs is confirmed by certificates of state registration of products.

ИЗГОТОВЛЕНО ПО ТЕХНОЛОГИИ ИХТТМ СО РАН

**Biocomposite "Immuno"** is a modern preparation of immunomodulating action with a high degree of bioavailability. It is created on the basis of mechanochemical technology, which allows to increase the effectiveness of preparations tens of times, increasing their absorption in the intestine.

**Biocomposite "Super Silicon"** is a preparation based on the chelate complex of silicon. It is made from vegetable raw materials, rice husk and green tea. Synthesis is carried out by mechanochemical activation of the components. In the course of mechanochemical synthesis, the reagents and products are in solid form, which allows preventing oxidation and loss of the biologically active components.

**Biocomposite "Alginat"** is a new effective preparation of complex action with a high degree of bioavailability. Mechanochemical technology provides the transition of calcium, magnesium, selenium, manganese, chromium and zinc from the inorganic phase to the water-soluble organic salt.

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# MECHANOCHEMICAL ABSTRACTION OF LATTICE OXYGEN FROM STABLE OXIDES BY ELECTROPHILES TOWARD FUNCTIONAL NANOCOMPOSITES

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Oxygen deficient oxide materials are of great technological significance. They are conventionally prepared either from stable oxides by heating under reducing atmosphere or from metals by sparingly oxidizing under controlled oxygen partial pressure. Oxygen abstraction by surrounding electrophiles is one of the established mechanisms of chemistry, explored comprehensively and utilized conventionally in many chemical processes including organic synthesis.

The abstraction is much more difficult in solid-states, since we need to attack lattice oxygen atoms, which are usually very stable in crystalline oxides, particularly those with highest oxidation number. Although related mechanisms are well explored in the interests of catalytic activity, they are not always taken over for the preparative methods for oxygen deficient metal oxides.

When electrophilic species like organic hydrocarbons are coexisting next to the oxide fine particles and mechanical stress is exerted on such a mixture, abstraction of lattice oxygen could take place at their contact points with simultaneous oxidative decomposition of the organic counterpart. Once oxygen is abstracted, oxygen vacancies are created to destabilize the oxides. Thus, the local reduction process becomes self-catalytic and penetrates the entire mass of the mixture.

By a proper choice of the mechanochemical condition and with subsequent chemical treatments, the rest of the organics could be eliminated or turn into various carbon-containing species, resulting in oxide-carbon-based nanocomposites. The properties of mechanochemically reduced oxides are substantially different from those prepared via a conventional route.

The presentation is based on the recent experimental studies carried out by the author and his colleagues mainly on $V_2O_5$, $SiO_2$ and $TiO_2$. Application of the products to the thermal energy storage and Li-ion anodes is briefly referred.

# MECHANICAL ACTIVATION OF REACTIVE SHS-MIXTURES AND SYNTHESIS OF MATERIALS

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Mechanical activation (MA) of reactive powder mixtures by means of intense treatment in planetary ball mills significantly influences reaction properties of reactive SHS-mixtures [1,2]. While data concerning combustion velocity and adiabatic temperature are contradictory, it is commonly agreed that MA results in decreasing of reaction onset temperature [3,4]. In this work, we consider influence of MA on the microstructure, onset temperature and reaction routes in the SHS-mixtures. Possible mechanisms of this effect, including storage of excess enthalpy, increasing contact surface area, cleaning of the contact boundaries, and formation of nanostructure product precursors are considered. A conclusion is made that formation of nano-sized precursors of the reactive products during intense sliding and shear deformation of the reactants causes abnormal reactivity of the mechanically activated SHS mixtures. It is shown that increasing reactivity of SHS-mixtures due to MA allows extending concentration limits of the combustion synthesis of materials. Prospective of using MA for producing materials with designed microstructure by SHS are outlined.

This work is supported by Russian Ministry of Science and Education, Grant № 14.587.21.0051.

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# ON THE KINETICS AND MECHANISMS OF REACTIONS INVOLVING MECHANICALLY ACTIVATED SOLIDS

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The reactivity of mechanically activated solids is assessed in terms of the changes in reaction kinetics. This paper is an overview which dwells on pros and cons of ‘model-based’ and ‘model-free’ approaches used to describe the kinetics. The reactions of mechanically activated solids with varying degree of complexity are covered: (a) simple dissolution reaction, ex. alkali leaching of boehmite ($\gamma$-AlOOH); (b) non-congruent dissolution with surface film formation, ex. alkali-leaching of zircon ($ZrSiO_4$); and (c) complex dissolution-precipitation reaction, ex. geopolymerisation of fly ash (coal combustion alumino-silicate residue). In the case of alkali leaching of boehmite, ‘model free’ analysis by iso-conversion method revealed that, depending on mechanical activation time the activation energy exhibits characteristic variation with fraction leached. The structural heterogeneity manifests in preferential dissolution and continuously changing nature of solid phase; consequently, rendering model-based analysis inadequate [1]. The alkali leaching of zircon is complex since mechanical activation not only enhances the leachability but simultaneously affects the film formation due to non-congruent nature of dissolution. ‘Model free’ approach fails to describe the kinetics since the nature of film changes with progress of leaching. Interestingly, the essence of leaching can be captured to a fair degree using ‘shrinking core model with film diffusion’ [2]. Geopolymerisation of fly ash is far more complex due to intrinsic chemical heterogeneity and mechanically induced structural heterogeneity. The importance of reaction path is highlighted using calorimetric maps. Model free analysis using iso-conversion method shows that the activation energy varies with fractional conversion and exhibits three regimes, indicative of different stages of geopolymerisation [3].

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# MECHANOCHEMISTRY OF ORGANIC COMPOUNDS. STATE OF THE ART AND CHALLENGES

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There is enormous industrial (and academic) interest in the use of mechanochemical methods. However, until more is known about their mechanisms, and the integrity of their results, their application in fine chemicals industries is greatly limited.

There is enormous industrial and academic interest in the use of mechanochemical methods in organic chemistry. During the last decade over hundred various transformations have been documented that range from polymorphic transitions and amorphisation to co-crystallisation, formation of salts, co-crystals, hydrates, as well as new chemical compounds, including, in particular, MOFs, or peptides.

Despite the widespread interest in the use of mechanochemistry, very little is understood about the mechanisms of mechanochemical processes. However, until this information is available, the application of mechanochemical methods in fine chemicals industries is greatly limited. The already documented transformations are not always reproducible, are difficult to control, to optimise and to scale up.

One of the main problems of organic mechanochemistry is that we do not often know that we do not know something important about the conditions, not only about the mechanisms of the transformation. In the present contribution I try to review the state of the art of research that helps one to answer the following basic questions:

- What are the experimental conditions (T, P)?
- Which chemical species and in which ratio participate in the reaction?
- Which products are formed?
- When and where are they formed?
- What is the reaction rate?
- What is the temperature dependence of the reaction rate?
- Is the process a solid-state process?
- Is the process in fact a result of mechanical action, and not of mixing of reactants and/or of creating fresh surfaces?

# TECHNOLOGICAL FUTURE OF MECHANOCHEMISTRY

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For the last three decades, the intensive investigations of mechanochemical effects did not result in a full-scale commercial technology. Any chemical technology consists in a combination of reaction conditions and well-specified equipment, which allow us to realize and to support these conditions in a reactor of sufficient capacity. Though the milling technologies are well known as the most large-scale processes, sometimes for millions ton per year, they cannot reproduce the laboratory conditions that are responsible for the mechanochemical effects.

Nevertheless, we observe the positive dynamics in this field. The new intensive mills appear in the market that can provide us up to 1-2 ton per hour of activated products. Taking into account that technological requirements sometime may be on this level or even much less, we can hope the development of commercial mechanochemical technologies in the nearest future. This is our duty. The four categories of processes we may consider as prospective:

1. *Powder technologies.* The direct mechanochemical synthesis of reactive powders such as carbides, pharmaceuticals, ceramics, etc., is now available for industrial applications in sufficient amounts. A good example is the production of special ceramic powder additives for cast iron modification, which has been realized in China by the license from ISSCM. The equipment in use is our mill of AGO-3 type.
2. *Mechanocomposites synthesis.* We have shown that mechanocomposites obtained by short-time mechanical activation, are very good precursors to be used in some thermal processes. The best example is the well-known mechanically activated SHS (MA SHS) applied to the synthesis of intermetallic compounds (not only). Thanks to *preliminary* MA the SHS conditions were optimized. As a result, the powder products became available from SHS. The variation of this technique is *thermal explosion* that allows us to get single-phase fine powder products. Evidently, this is a technological breakthrough to small and medium-scale industrial products.
3. *Polymer (plastic) composites production.* This is a large-scale industry in the world. Practically all plastics use powders for fillers. The properties of final materials depend strictly on how uniformly these fillers are distributed in the mass of polymers. This typical mechanochemical problem is not solved yet because of lack of high capacity mills for plastic materials treatment.
4. *Natural products treatment.* This is the very wide and attractive field for industrial applications of mechanochemistry. Biologically active products obtained by extraction, *mechano*-fermentation, or directly by efficient milling process were realized already for some commercial products. This kind of technologies is also interesting for numerous agricultural wastes, which can be easily transformed into useful products with rather simple mechanochemical technologies.

# NEW INSIGHTS IN MECHANOCHEMICAL PROCESSES USING REAL-TIME IN SITU INVESTIGATIONS

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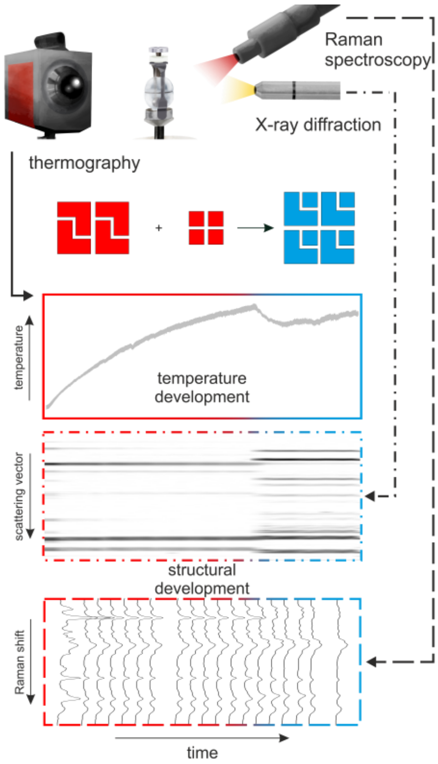

Mechanochemistry is a fast and efficient method applicable for the synthesis of new organic [1], metal-organic [2], and inorganic [3] compounds. The direct monitoring of milling reactions is still challenging. The underlying reaction mechanisms remain often unclear. In the last years, a tandem in situ approach for investigating mechanochemical reactions using time-resolved in situ XRD coupled with Raman spectroscopy [4] has been established. Here, we present an in situ coupling of synchrotron XRD, Raman spectroscopy, and thermography allowing the observation of mechanochemical reactions in real time [5]. Information on the crystalline, molecular, and temperature state of the materials during grinding could be collected. The chemical composition of the reaction mixture was found to be directly correlated with changes in the temperature profile of the reaction. Furthermore, the presented setup allows the detection of crystalline, amorphous, eutectic as well as liquid intermediates. The resulting deeper kinetic and thermodynamic understanding of milling processes is the key for future optimization of mechanochemical syntheses.

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# THE MECHANOCHEMICAL MODEL EXPERIMENTS OF IMPACT COMPRESSION AND IMPULSE LASER HIGH-TEMPERATURE HEATING

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An elementary act of mechanochemistry is the impact of a ball on an activated system, consists of several stages, including mechanical shock compression and high-temperature heating. Each stage lasts for several microseconds. The purpose of this work was to put model experiments simulating these stages. Mechanical compression can be simulated with using a gas-dynamic gun, and high-temperature heating with using a high-power pulsed laser. As a result of this action, processes are initiated in the sample (adiabatic compression and heating, development of thermal stresses, increase of pressure in the local region), which creating extreme conditions (maximum T~10000 C, P ~ 1 million atmospheres), leading to structural changes associated with chemical reactions, phase transitions, the destruction of the material. These processes are so unusual, and difficult for research because of the lack of appropriate instruments, that the nature of these phenomena occurring only under extreme conditions is unknown to date.

**Methods of research.** Three research methods were implemented: the X-ray imaging, the small-angle X-ray scattering (SAXS), and the X-ray diffraction. The X-ray imaging is used to tomographically reconstruct the density distribution in the sample during shock wave compression, to investigate ejected products density distribution in spallation processes. Small-angle X-ray scattering is used to study the nucleation and growth of nanoparticles - the products of a chemical reaction during shock wave compression (for example, nanodiamonds, nanoparticles of metals), is used to analyze the size of the particles formed during ejection in spallation processes. X-ray diffraction is used to study the change in the crystal structure of samples, simulated by laser pulse with parameters: E = 100 J, duration 120 microseconds.

**Results**: equation of states was received for several materials, nucleation of new phase during compressing was investigated, development of temperature front, stress and cracking was investigated during laser heating.

# APPLICATION OF MECHANICALLY-ACTIVATED SHS FOR THE SYNTHESIS OF SOLID SOLUTIONS IN THE QUSI-BINARY SYSTEM TaC-ZrC

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Solid solutions in the TaC-ZrC system attract wide interest as the prospective materials for aerospace industry. These solutions possess high melting temperatures, hardness, resistance towards erosion and ablation. However, synthesis of the single-phase solid solutions TaC-ZrC is problematic due to the extremely high melting temperatures and low coefficients of self- and hetero-diffusion of TaC and ZrC. Self-propagating high-temperature synthesis (SHS) has been proven as an effective alternative for the traditional powder metallurgy methods in the field of refractory ceramics, including the ones with complex chemical composition. However, initial experiments related to SHS in Ta-Zr-C system demonstrated that due to the high heterogeneity of the reaction mixture as well as insufficient thermal relaxation duration of combustion products the diffusion between TaC and ZrC is impeded and the single phase solid solution does not form.

However, it is known that application of preliminary mechanical activation (MA) allows one to optimize the conditions of SHS processes and properties of the synthesized products. MA was applied to Ta-Zr-C mixtures with a dual goal: first, to increase the reactivity of the mixture, and second, to decrease the heterogeneity scale of the reaction mixture and increase the effectiveness of diffusion processes in the combustion wave. Optimal regimes of MA SHS were found, allowing the synthesis of single-phase TaC-ZrC solid solutions with various compositions.

This work was supported by the grant of Russian Science Foundation (project № 17-79-10173).

# SYNTHESIS OF ALUMINUM AND MAGNESIUM DIBORIDES BY THERMAL EXPLOSION IN MECHANICALLY MILLED POWDER MIXTURES

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Boron possesses the highest heat of combustion per unit mass and unit volume among the elements of practical significance and could serve as a high-energy additive to solid fuels for ramjet engines. However, the formation of an oxide layer on the surface of boron particles slows down the oxidation process and the rate of heat evolution. Because of this shortcoming of boron, magnesium and aluminum diborides are currently considered to be more suitable as high-energy additives. $MgB_2$ and $AlB_2$ are usually synthesized by prolonged annealing of the reaction mixtures at temperatures exceeding 1000 ºC.

The goal of this work was to develop a low-temperature synthesis method of aluminum and magnesium diborides having crystallites in the nanometer range.

The method uses mechanical milling of reaction mixtures in a planetary ball mill, which is followed by igniting a self-sustaining reaction in the thermal explosion mode. Reaction mixtures were prepared using Al (PA4, 98% purity), Mg (MPF-3, 99% purity) and amorphous boron (B 99A, 99.3% purity) powders.

Conditions of mechanical milling ensuring a reduction of the ignition temperature of thermal explosion to temperatures below the melting points of aluminum or magnesium have been found. The products of thermal explosion are $AlB_2$ and $MgB_2$ with trace amounts of $Al_2O_3$ and MgO, respectively.

Additional mechanical milling of the synthesized diborides allows reducing the size of their crystallites to the nanoscale.

Results of the X-ray phase analysis and electron microscopy studies of the mechanically milled powders mixtures as well as products of thermal explosion will be reported.

# MECHANICAL ACTIVATION AND THERMAL EXPLOSION IN A LOW-CALORIE POWDER MIXTURE Nb + 2Si. EXPERIMENT AND MATHEMATICAL MODEL

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Experimental studies of mechanical activation (MA) and thermal explosion (TE) in the Nb – 2Si system were carried out and a mathematical model of the process was developed. It is shown that mechanical stimulation intensifies the phase formation in the powder mixture and promotes fuller transformation into a reaction product of stoichiometric composition.

The powder mixture of $NbSi_2$ stoichiometry was mechanically activated in a planetary high-energetic (60 g) centrifugal mill from 1 to 60 minutes. Then the thermal explosion of the MA-composition was carried out at a constant volume unit in the argon medium and the temperature characteristics TE were fixed.

It was established that the MA of the powder mixture intensifies the chemical transformation, which leads to the formation of a multiphase product with the formation of both stoichiometric and intermediate phases. With the extension of time of MA, at TE of mechanically activated mixture, the ignition temperature increases, reducing the maximal temperature of synthesis and the magnitude of the heat effect of the formation of reaction product. There is a change of the TE mode: up to 5 min of MA, the reaction is carried out with the participation of the melt, after 5 min of MA the interaction occurs in solid state. Time limits of the MA for realization of thermal explosion were defined.

A mathematical model of synthesis by TE in a mechanoactivated heterogeneous system is developed. The model takes into account the change in the main characteristics of the process: temperature, depth of chemical transformation, the value of the area of the interphase surface and contained in the structural defects of excess energy. Using experimental data, thermophysical and thermokinetic constants characterizing the process of two-stage mechanochemical synthesis in the systems are determined by the inverse problem method. Numerical calculations correspond to the results of experiments.

# MODEL OF COMBUSTION OF MECHANICALLY ACTIVATED Ti-C, Ti-B, Ti-Si POWDER MIXTURES

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To study the dynamics of reaction front formation, in this paper, the process of composites synthesis in the systems Ti-C, Ti-Si, Ti-B is investigated numerically taking into account the reaction retardation due to the reaction product accumulation with the help of special kinetical function.

The mathematical models of reaction initiation in powder mixtures consisting of titanium and graphite, titanium and boron, titanium and silicon are considered. The sample is the cylinder of radius *r* consisting of two powder layers. The first layer (igniter) is a stoichiometric mixture of Ti and Si powders, and the thickness of this layer is *l*. The second layer of thickness *L* is non-stoichiometric powder mixture of Ti with carbon C (carbon black) or Ti with B or Ti with Si. Here the titanium is presented in excess, so that it is not completely consumed in the reaction. Based on experimental information found in the literature the detailed mechanism of the chemical conversions in the system is taken into consideration. It is known that in non-stoichiometric mixtures the self-propagation mode can be impossible, because chemical heat release is not enough for this mode. To proof this situation mechanical activation was used. It leads to active surface appearance and apparent decrease of activation energy. Additionally, some physical properties can be changed. To take into account the mechanical activation influence the additional parameter is introduced in the combustion model. This is activation parameter calculated from activation volume change.

The melting of species, properties evolution during reaction, the heat losses to the environment by convection (if the synthesis is carried out in an inert gas atmosphere) and by thermal radiation are taken into account also.

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# TOWARDS UNDERSTANDING MECHANICAL EFFECTS IN SOLIDS: APPLICATION OF HIGH PRESSURE STUDIES

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The last decade has shown enormous interest in various mechanical effects arising on chemical reactions and polymorphic transformations. The structural changes accompanying a solid-state chemical reactions and phase transitions depend strongly on the mechanical properties of the sample, which can differ even for isostructural and chemically related compounds. Many of these reactions are accompanied by various mechanical effects, including bending, twisting, curling, jumping of crystals. Creating high hydrostatic pressures is one of the most efficient methods for analyzing the response of a crystal structure to external stress. Combining photo- and thermo- crystallography with high-pressure research can have a synergetic effect when elucidating the mechanisms of the effects. Single-crystal to single-crystal transformations are of special interest in this case since they make it possible to follow structural strain by optical microscopy to directly see the mechanical response and crystal shape changes.

In this contribution we discuss the experimental results obtained for several classes of compounds showing photomechanical and thermomechanical effects: Co(III) complexes with general composition $[Co(NH_3)_5NO_2]XY$ (where X, Y = $Cl^-$, $Br^-$, $I^-$, $NO_3^-$) undergoing UV or visible light-induced photoisomerization to give $[Co(NH_3)_5ONO]XY$ as products; a series of rare-earth element hydrated oxalates $(REE)_2(C_2O_4)_3\cdot 10H_2O$ (REE = Sm, Y) undergoing dehydration to $(REE)_2(C_2O_4)_3\cdot 6H_2O$ with crystal shape change on slight heating with pronounced thermomechanical effects; organic molecular crystals undergoing phase transitions on changing temperature accompanied with significant mechanical response of the crystal (*e.g.* 1,2,4,5-tetrabromobenzene). Crystal structures have been studied by single-crystal diffraction on irradiation, at variable temperatures and high pressures *in situ*. The data on structural changes (anisotropic strain, molecular rearrangements, structural phase transitions and chemical reactions) under different conditions have been analyzed.

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# FOLLOWING THE KINETICS OF SOLID STATE PHOTOCHEMICAL REACTION BY MEASUREMENT OF MACROSCOPIC MECHANICAL RESPONSE IN CRYSTALS

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Photochemical reactions can cause macroscopic mechanical effects when occurring in crystals. The deformation is the external manifestation of internal change of molecular conformation and intermolecular interactions caused by the reaction. It can be considered as a mechanical response to the reaction. The magnitude of the response can be quite large in case of needle shaped crystals with thickness compared to the irradiation penetration depth. The reaction non-uniformity due to light absorption leads to a remarkable crystal bending. For single-crystal-to-single-crystal transformations, provided that certain conditions are fulfilled, the magnitude of the response, like the curvature of bending crystal, can be a measure of the transformation degree.

Reversible $NO_2$-ONO linkage photoisomerization was studied in thin needle-like crystals of $[Co(NH_3)_5NO_2]$ Cl $NO_3$. Measurement of the crystal elongation and curvature changing in course of the reaction allowed high-precision determination of the kinetic parameters of the quantitative model of the reaction. Temperature dependencies of the quantum yield of the photoisomerization and of the reverse thermo-isomerization reaction, as well as the compositional (nitro/nitrito) dependencies of the quantum yield and of the light penetration depth have been found. We illustrate how the kinetic constants and their temperature dependencies can be found with high precision for the direct photochemical and for the reverse thermal transformations. We also show the possibility to detect the feed-back phenomenon and to characterize it quantitatively.

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# PRESSURE EFFECT ON THE STRUCTURE AND ELECTRONIC PROPERTIES OF OXYANIONIC CRYSTALS FROM FIRST PRINCIPLES

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Nitrates and perchlorates are oxyanionic compounds that are used as energetic oxidizers in propellants, in explosive and pyrotechnic systems, and as sources of oxygen in breathing apparatus. Interfacial disruption of adhesion in solid propellants is regulated by the behavior of damages such as cracks. It is known that strong compressibility anisotropy can lead to the appearance of microcracks. Shock waves, passing through an explosive during detonation at high speed, can generate high pressure within the material. It is considered that the status of energetic materials under extreme conditions greatly influences the detonation reactions. Investigations of the behavior of solids under pressure are necessary not only for understanding the mechanisms of mechanochemical processes, but also very promising as one of the powerful methods for studying intermolecular interactions [1]. Density functional theory (DFT) proved to be quite efficient in the simulation and prediction of the physical and chemical properties of a wide range of materials. In the present work, a first-principles study within DFT of the pressure effect on the structural and electronic properties of nitrates, perchlorates, and oxyanionic hydrates has been carried out [2, 3]. As a result of the calculations, compressibility anisotropy is established, which is due to the anisotropy of the chemical bond. It is found that the expansion of hydrogen bonds correlates with the negative linear compressibility of organic cation nitrate DATN and with the metal-organic framework crystal [Ag(ethylenediamine)]$NO_3$, while the deformation of Ow-H···O hydrogen bonding motifs correlates with the negative linear compressibility of oxyanionic hydrates [2,3]. NLC materials are very much desirable for applications, such as ultrasensitive pressure detectors, shock resistance materials, artificial muscles, body armor, pressure switches. The band gap of DATN nonlinearly decreases with pressure. In contrast to trihydrates, monohydrate band gap increases with pressure.

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# DESCRIPTION OF POLYMORPHOUS TRANSFORMATIONS IN METALS ON THE BASIS OF THE CLUSTER MODEL OF STRUCTURAL FORMATION

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The work deals with the processes of structure formation that take place during polymorphic transformations in metals. From the positions of the cluster approach to structure formation, a model of polymorphic transitions in metals with FCC, HCP, and BCC lattices is proposed. The model is based on the idea of preserving the volume of the octahedral cluster elements of the corresponding lattices. The calculations made show a good coincidence of the calculated data with the model representations proposed in the paper.

The method shows good results when analyzing both pure metals and some alloys. It is known that during plastic deformation many alloys experience polymorphic (martensitic) transitions. The phase transition in ferromanganese alloys with a manganese content of 15% is considered. In this alloy, solid manganese solutions in crystalline lattices based on α- (BCC), γ- (FCC) and ε- (HCP) iron can be present. The result confirms the adequacy of the model with an error not exceeding 3%.

# MOLECULAR DYNAMICS RESEARCH OF NANO-SIZED ROD FAILURE AT THE CYCLIC LOAD

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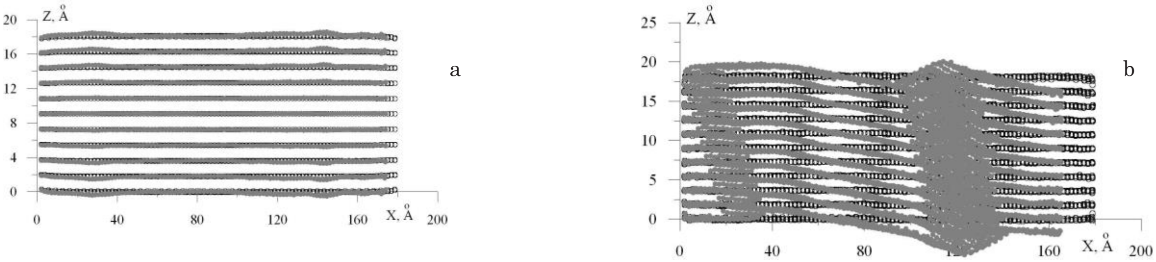
The aim of this work is the research of temperature influence on nano-sized rod failure at cyclic load. The perfect copper crystal shaped as a rectangular parallelepiped was used as a physical system; the number of crystalline cells in it is $n_x = 50$, $n_y = n_z = 5$ along respective axes. The EAM potential is used to simulation inter-atomic interactions. The well-known Verlet velocity modification of the second-order accuracy, with the time pitch of $10^{-16}$ s is used.

The external force is applied to each atoms of right edge of nano-sized rod in order to simulate cyclic stress action to right free tip of rod:

$$f_{ax} = -\sigma S / n_f$$

$S$ – the area of the last atomic plane on the right, $n_f$ – the number of atoms on this face, $\sigma = \sigma_0 \cdot \sin \omega t$ .

The temperature has strong effect on the rod fracture at the cyclic load. It is clearly visible in exterior view of the sample (see figures below).



The nanostructure outlook in the plane XZ. $\sigma_0$ =1GPa, $N_\omega=10^5$, ν=1 THz. Black bubbles – the initial placement of atoms, grey bubbles – the placement of atoms in the time moment 50 ps. (a) $T_0 = 0$ K; (b) $T_0 = 100$ K.

It was revealed that the dispersion of the *x*-coordinate, which describes the root-mean-square deviation of atoms of fixed atomic plane from its mean coordinate in the time moment $t$, is the best criterion of the failure of ideal atomic planes.

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# EFFECT OF PROCESSING METAL-MATRIX SHS POWDERS IN A PLANETARY MILL ON DISPERSION, MORPHOLOGY, PHASE COMPOSITION AND FINE PHASE STRUCTURE

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Mechanical activation (MA) of reaction mixtures on the basis of metal powders is usually used to extend concentration limits of wave mode SHS or to reduce combustion temperature down till solid-phase combustion mode. When there is a metal excess in metal – nonmetal powder mixtures SHS products represent metal matrix composites (MMC). MMC structure corresponds disperse particles of hard compounds (carbide, boride, silicide) imbedded into metal matrix (binder). Disperse compound particles serve as strengthening phase in the composite. Less is size of the particles more is the strengthening effect. MA is an effective method to reduce strengthening phase size in metal matrix composites.

TiC+Ti binder MMC have been investigated in our work. The composites were produced via three steps route: TiC powder synthesis by SHS in titan and black carbon powder mixtures → intensive processing SHS TiC powder in a planetary mill (MA) to get submicron size powder → blending of Ti powder with MA treated TiC powder and MA retreatment of TiC+Ti powder mixture. The target of described above treatment is to get titanium matrix composite powders reinforced with submicron carbide particles. The composite powders can be used for cladding or sputtering of wear resistance coatings and in additive technologies.

Morphology, structure and phase composition of the MA treated powders were investigated by X-ray diffractometry, scanning electron microscopy and electron probe analysis. It has been found that after proper intensity of MA treatment the composite powder particles shape becomes sphere-like with size from microns to tens microns. Submicron TiC particles are embedded into surface layer of the composite powders. So there is no segregation in the mixtures of Ti and Ti powder of different size and density.

# EFFECT OF MECHANOACTIVATION ON THE HIGH-TEMPERATURE BEHAVIOUR OF THE SYSTEMS WITH METASTABLE PHASES

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During mechanoactivation of solid-phase mixtures, grinding and plastic deformation of substances occurs, mass transfer is accelerated, mixing of the mixture components at the atomic level is carried out, and their chemical interaction is activated [1]. In metal alloys reduction of crystallite sizes is accompanied by suppression of martensitic transitions [2]. As a result of the mechanical action, the stress field is created in the contact areas of the solid. Its relaxation may occur through the release of heat, the formation of a new surface, the formation of various defects in crystals, the excitation of chemical reactions in the solid phase. Mechanoactivation processes can also lead to the appearance of new types of metastable phases due to the redistribution of cations among crystallographic nonequivalent sublattices [3].

In this work, the influence of mechanoactivation on the high-temperature behavior of systems with metastable phases is analyzed. Comparison of structural phase transformations in the conditions of temperature growth in various oxides subjected to mechanochemical activation and structural characteristics of the resulting crystalline phases allows us to estimate whether the previously established regularities are common for systems with different types of chemical bond. The influence of mechanical activation on structural phase transitions of both the martensitic type (for example, from the cubic into the tetragonal modification in $Mn_3O_4$) and accompanied by redox processes (between phases with different oxidation degrees, etc.) is considered. It is shown that, despite the relaxation character of the evolution of the metastable structures, the obtained temperature shift of the corresponding phase transitions takes place together with changes in the structural characteristics of the formed new phases in comparison with the initial oxides.

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# EFFECT OF MECANICAL ACTIVATION ON $Al(OH)_3 \rightarrow \alpha\text{-}Al_2O_3$ TRANSFORMATION

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Thermal treatment of aluminum hydroxide at little more than 1200°C leads to a thermodynamically stable $\alpha$-$Al_2O_3$, the latter being extremely widely used in industrial applications. Unfortunately, high temperature of the transformation results in a coarse powder with a vermicular particle shape that cannot be used in ceramics without intensive and prolonged milling. At the same time, it is known that high energy milling of $Al(OH)_3$ causes its amorphization and decrease the temperature of α-alumina crystallization down to 900°C. HRTEM discovered 2-3nm areas of α-alumina structure in mechanically treated hydroxide. Supposing that these areas serves as seeds facilitating above mentioned transition, an attempt to make the process applicable in industry, that is to lower the intensity of milling by seeding hydroxide with $\alpha$-$Al_2O_3$ nano-particles, has been made in the present work.

It was shown that 20min milling a mixture of gibbsite and 1-5 wt.% of α-alumina nano-particles with crystallite size of 15, 25, or 50 nm in AGO-2M brought about the fall of $Al(OH)_3 \rightarrow \alpha\text{-}Al_2O_3$ transformation temperature down to 800-900°C and the resulting powder has particle size within interval of 50-90nm depending on the amount and size of added seeds. As soon as the acceleration developed in the mill exceeds or equal to 10g a complete transition to α-alumina was achieved within 20-30 min heating on air. Although having low particle size, the product exhibits poor sintering behavior due to its aggregated nature which could not be improved by any ordinarily used methods. Nevertheless the process of aggregates formation has been successfully suppressed by changing gas atmosphere at which crystallization was carried out and eventually rounded particles of about 100nm have been produced. Dry CIP at 200 MPa was applied to compact a green body that sintered to more than 98% of theoretical density at 1350°C.

Rough quantitative estimation has been made to get a conclusion that the effect achieved in planetary mill at 10g can be reproduced in a tumbling mill provided it has a diameter larger than 50cm, though for a much longer time. 30h milling in the tumbling mill partially confirmed the estimation since 100% transiton to $\alpha$-$Al_2O_3$ has been achieved at 1000°C and the product possessed high sinterability as well.

# MECHANISMS OF FORMATION OF PHASES AT MECHANOSYNTHESIS OF Fe-C ALLOYS

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The study of the regularities of the formation of phases during mechanical alloying of mixtures based on the compositions of Fe95C5, Fe83C17, and Fe75C25 was carried out. The main phases forming powder alloys are cementite, amorphous phase and ferrite. In Fe75C25-based alloys, it is also possible to form other carbides - Fe5C2 and Fe7C3. The last phases are formed under the influence of impurities O and N.

Mechanical alloying in the Fe-C system begins with the formation of a nanograin state of ferrite with developed segregation of carbon along nonequilibrium boundaries. On this basis, an amorphous phase is formed. The formation of carbides with a trigonal-prismatic environment of carbon atoms having a complex crystal lattice occurs predominantly through the amorphous phase, and close-packed phases with a simple crystal lattice are formed without its participation.

Thermally activated processes play an important role in phase formation during mechanosynthesis. The formation of phases in Fe-C-based alloys largely occurs as a result of processes associated with the relaxation of excess energy accumulated during deformation. These processes tend to bring the system into a state of equilibrium, which is reflected in the tendency to establish phase compositions determined by the conditions of stable or metastable equilibria. Studies of the kinetics of phase formation in Fe75C25-based alloys have established that the interaction of phases at various stages of mechacal alloying can be described from the point of view of dynamic phase equilibria.

The phase formation that takes place in the Fe-C system in such essentially nonequilibrium processes as the tempering of martensite, iron saturation with carbon from the gaseous medium, the deposition of films, quenching of the melt, and severe plastic deformation are described within the framework of general laws. This is manifested thermodynamically in the formation of metastable phases due to the high chemical potential of the components of the system, and kinetically in the formation of phases that have the most favorable conditions for nucleation.

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# MECHANOCHEMICAL SYNTHESIS OF METAL NANOCOMPOSITES AND CARBIDES

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It is known that, due to their high melting temperature, electrical, and thermal conductivity, metal carbides are widely used as materials for aviation and space industries. Hafnium carbide is a highly effective electron collector. It can be used to produce thermionic electrical power generators and the parts of powerful ion engines. Hafnium carbide ($T_m$ = 3960°C) is used to produce the nozzles of space rockets and some structural elements of gas-phase nuclear jet engines.

Hard alloys based on titanium carbide are promising materials for the manufacturing of structural parts (bearings, seals, etc.) of the friction units operating at temperatures up to 1100°C.

The mechanically triggered interactions in the Ti – C and Hf – C systems performed in a high-energy planetary ball mill are studied. The formation of carbides (TiC, HfC) in the course of mechanochemical synthesis at the different stages is followed by both conventional and synchrotron X-ray diffraction analyses and high-resolution scanning electron microscopy. The interaction between metallic Ti (Hf) and C proceeds through the formation of mechanocomposites Ti/C (Hf/C) at the first stage, followed by the melting of titanium (hafnium), its spreading over the carbon particle surface and the crystallization of titanium (hafnium) carbides.

Under the present conditions, the relatively rapid mechanosynthesis of TiC and HfC is completed after 4 and 8 min of mechanical activation, respectively.

# MECHANOCHEMICAL SYNTHESIS OF TERNARY PEROVSKITE $Pb_2InNbO_6$

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The influence of mechanical activation on the synthesis and properties of the lead indium niobate ceramics $Pb(In_{0.5}Nb_{0.5})O_3$, which can be used as piezomaterial and piezoelement to manufacture measuring devices, has been investigated. High-energy mechanical activation was carried out using planetary-centrifugal mill AGO-2 at ball acceleration of 40g. The powder to balls mass ratio was 1:20; balls diameter was 8 mm.

Weighted portions within 1 g were taken; samples were pressed as tablets 10 mm in diameter and about 2mm thick. The samples were pressed without a plasticizer using a hydraulic press at the pressing force of 10 t/cm$^2$.

As a result of investigation, the possibility to obtain $Pb(In_{0.5}Nb_{0.5})O_3$ from mechanochemically activated and previously annealing precursors of the samples was demonstrated.

At the samples activated within 10 minutes, the structure perovskite remains at roasting in the range of temperatures 900°C - 1100°C.

In the same interval of temperatures samples have also the maximum density.

The samples activated within 20 minutes, have pure perovskite no structure.

The least quantity of a pirochlore phase is present in samples sintered at temperature 900°C and 1000°C.

At grinding of samples the quantity of a phase pirochlore does not change.

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# MECHAHOCHEMICALLY STIMULATED SYNTHESIS OF α-$LiAlO_2$

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For fuel elements with carbonate-melt electrolyte, the fine low-temperature modification of α-$LiAlO_2$ is the most efficient material for the matrix electrolyte. The indicated monoaluminate should meet definite requirements to specific surface (not less than 10 $m^2$/g) and have a bimodal particle size distribution. Mechanochemically stimulated synthesis, which had been successfully applied previously to obtain γ-$LiAlO_2$, has essential advantages over the traditional methods of obtaining monolauminates, ceramic and sol-gel procedures. It involves the joint mechanical activation of a mixture of reagents ($Al(OH)_3$ and $Li_2CO_3$), followed by their thermal treatment in the air.

The goal of the present work was to study the processes involved in the synthesis of fine dispersed α-$LiAlO_2$ through the thermal treatment of a mechanically activated mixture of $Al(OH)_3$ and $Li_2CO_3$ in the laboratory activator of planetary type, and to investigate the possibility to implement this process at a larger scale than the laboratory one.

The obtained experimental data show that the mechanical activation of a mixture of gibbsite and lithium carbonate in the planetary activator AGO-2 at the centrifugal acceleration of 10 g for 1 min and subsequent thermal treatment at a temperature of 650 to 700 °C in the air leads to the formation of practically monophase fine α-$LiAlO_2$. The specific surface and particle size distribution of the resulting aluminate allow using it as a material for the matrix electrolyte in carbonate-melt fuel elements. The soft conditions of mechanical activation, necessary for the synthesis of α-$LiAlO_2$ and not leading to X-ray amorphous aluminium hydroxide, allow one to use not only planetary-type activators for the synthesis but also other apparatuses including continuous-type ones, possessing higher productivity.

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# MECHANICALLY STIMULATED THERMAL SYNTHESIS OF LITHIUM ALUMINATES

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Fine-particle lithium aluminates (α, γ-$LiAlO_2$) with a specific surface area $S \geq 10$ $m^2$/g find application as an electrolyte matrix material for molten carbonate fuel cells, in lithium thermal batteries, to modify the conductivity of lithium polymer electrolytes, and to produce ceramic membranes for lithium ion batteries. Standard ceramic processing techniques for lithium aluminates synthesis, through the calcination of a mixture of lithium salts and aluminum compounds, require rather high temperatures and a long time and lead to the formation of a final product with a small specific surface area. To intensify the process of interaction between the reagents, it is possible to use preliminary mechanical activation of the reagent mixture in planetary activators with subsequent heat treatment of the activated mixture. The influence of the conditions of preliminary mechanical activation of a mixture of gibbsite and lithium carbonate in activators of planetary type and the conditions of subsequent heat treatment on the phase composition and specific surface of lithium aluminates is studied. It is shown that complete amorphization of gibbsite during mechanical activation and heating of the activated mixture in air above 800 $^oC$ leads to the formation of highly dispersed γ-$LiAlO_2$. Thermal treatment of a mechanically activated mixture in the atmosphere with a partial vapor pressure of water below 0.1 Pa allows the synthesis of γ-$LiAlO_2$ without significant amorphization of gibbsite. For the synthesis of α-$LiAlO_2$ preliminary mechanical activation should not lead to the amorphization of aluminum hydroxide, and the process of heat treatment should be carried at high partial vapor pressure of water ($P_{H2O}$>1200 Pa) and temperatures below 700 °C. The mechanism of formation of highly disperse lithium aluminates during mechanical activation and subsequent heat treatment of a mixture of gibbsite and lithium carbonate is discussed.

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# HIGH-DISPERSED POWDERS OF COPPER AND MOLYBDEN OBTAINED BY MECHANOCHEMICAL REDUCTION OF THEIR OXIDES BY MAGNESIUM

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Superfine powders of copper and molybdenum are used in the production of a wide range of modern materials with the necessary physicochemical characteristics. Mechanochemical process has economic potential, since it differs not only in short synthesis times, but also in eliminating a number of problems related to environmental pollution. Mechanical activation of solid mixtures leads to mechanochemical interactions and ultimately to the formation mechanocomposite ($Me/(Me_{akt})_xO_y$).

The influence of the conditions of mechanochemical reduction (the activation time, loading, stoichiometry) of copper and molybdenum oxides by magnesium on the formation of Cu/MgO or Mo/MgO mechanocomposites was studied in this work. It was also investigated the subsequent separation of superfine copper and molybdenum powders from magnesium oxide contained in mechanocomposites.

By means of X-ray phase analysis, IR- spectroscopy, electron microscopy and energy dispersion analysis, it is shown that the mechanochemical reduction of copper and molybdenum oxides by magnesium is completed by 2 minutes of activation for copper and by 8 minutes for molybdenum. The main products of reduction are mechanocomposites Cu/MgO and Mo/MgO.

Studies of separation of copper and molybdenum from magnesium oxide were carried out by the action of dilute acids on mechanocomposites (Me/MgO). The obtained ultra disperse powders of copper and molybdenum consist of aggregates of primary particles, almost spherical in shape and ~ 50-100 nm in size, which are part of secondary particle aggregates with dimensions from 0.2 to 10 μm.

The conditions for the protection of highly dispersed copper and molybdenum powders from oxidation are determined. The powder diffraction patterns, the shape and size of the powder particles do not change during storage under normal conditions for 1-2 months.

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# NEW SOLID-PHASE METHOD OF SYNTHESIS OF POLYOXOMETALLATE COMPOUNDS OF MOLYBDENUM

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For many years, the polyoxometallate complexes of the d-elements of the VI group of the Periodic System attract the close attention of researchers. Interest in these substances is primarily due to the possibility of using them as precursors of effective catalytic systems, catalysts and biologically active compounds. Polyoxometallate complexes often form unique supramolecular ensembles that have unusual spectral and magnetic characteristics. Such polyoxometallate complexes include molybdenum blue, which is a mixture of nonstoichiometric molybdenum compounds, in which the degree of oxidation varies from +5 to +6. To obtain such systems and their practical use, effective and reliable methods of synthesis are needed.

Despite the fact that molybdenum blue is known and widely used for almost 200 years, little attention has been paid to the development of synthesis methods. In general, the data available in the literature refer to the production of crystalline precipitates and films by reducing molybdenum (VI) compounds in an acid medium ($pH \leq 3$).

At the heart of the proposed new approach to the synthesis of molybdenum blue is the use of preliminary mechanical activation of natural molybdenite to generate surface oxide structures, which upon subsequent absorption of molybdenite from the atmosphere, will form molybdic acids on the surface. The use of the mechanoactivation method makes it possible to synthesize molybdenum blue in the molybdenum-containing reagent-reducing agent system, which in turn leads to a significant reduction in the complexity and time of production.

# MECHANICAL ALLOYING BY HIGH PRESSURE TORSION OF BINARY SYSTEMS BASED ON FCC METALS

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The effect of cryogenic temperature on the formation of solid solutions by mechanical alloying was studied using some structural analyses such as synchrotron radiation diffraction, Mössbauer spectroscopy, etc. and microhardeness measurements. Systems characterized by different enthalpy of mixing including Cu-Ag, Cu-Fe, Au-Co and Cu-Zn were involved. To realize mechanical alloying it was exploited a severe plastic deformation technique known as high pressure torsion. For majority of the bimetallic systems the severe plastic deformation was realized at room and liquid nitrogen temperatures. The components were in condition of powder mixtures before the deformation.

By using synchrotron radiation diffractometry it was found that for Au-Co characterized by a positive enthalpy of mixing (+20 kJ/mol), the cryogenic high pressure torsion resulted in higher content of dissolved Co compared to the cold high pressure torsion. For 80:20 at.% composition there have been a solid solution formation, correspondent to the composition of the respective original mixture. By the way, for Cu-Ag system with a low positive enthalpy of mixing (+5 kJ/mol) of 80:20 – composition, at. %, there has been the opposite effect from cryogenic deformation which consisted in a less dissolution. The same was for Cu-Zn of 80:20 at. % composition characterized by negative mixing enthalpy (- 6 kJ/mol). Finally, for Cu-Fe system the formation of nanocrystalline structure and non-equilibrium solid solution state was observed using nuclear gamma resonance method for 80:20 and 20:80 at. % compositions. The last system characterized by the largest positive mixing enthalpy of the components (+60 kJ/mol) among the present systems.

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# REDISTRIBUTION OF ALLOYING ELEMENTS (Cr, Ni) IN MECHANOSYNTHESED ALLOYS OF THE COMPOSITION OF CEMENTITE

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X-ray diffraction, Mossbauer spectroscopy, and magnetic methods have been used to investigate the processes of mechanical alloying in compounds $(Fe_{1-x}Cr_x)75C25$ and $(Fe_{1-y}Ni_y)75C25$, where x = 0.01-0.1, y = 0.05-0.2. Powders of pure metals and graphite were used as starting materials. The choice of alloying elements was due to the fact that chromium and nickel in their properties are close to iron, so they are able to easily replace iron atoms in the α-Fe lattice and amorphous phase. At the same time, chromium, being strong carbide-forming agent, has a high solubility in cementite, and nickel, as a weak carbide-forming agent, is low solvable. These circumstances make it possible to investigate features of the redistribution of the components of alloys between phases in the process of their formation during mechanical melting.

The fusion of the components of Fe-Cr-C mixtures in the early stages leads to the formation of an amorphous phase. Chromium interacts with other alloy components gradually. Therefore, in the initial stages, the amorphous phase has a low chromium content. At the same time, it is heterogeneous and consists of volumes depleted and enriched in chromium. On the basis of the amorphous phase, cementite is formed, mainly due to the chromium-enriched component. The remaining amorphous phase is depleted of chromium. As chromium is involved in the fusion, the chromium concentration in both phases rises and the chromium content in phases becomes closer.

In nickel-doped alloys in the initial stages of mechanical alloying, the heterogeneity of the amorphous phase is also observed. In this case, cementite is formed mainly on the basis of nickel-depleted regions, it dissolves less than 3-4 at. % Ni. The amorphous phase is enriched with nickel. The heterogeneity of the phases in terms of nickel content is maintained high throughout the entire mechanical alloying process.

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# SURFACE MODIFICATION OF Fe-Si-Al ALLOY UNDER WET BALL MILLING

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Finely dispersed particles of soft magnetic Fe-Si-Al alloys are widely used as fillers of magnetodielectric composites for high-frequency applications due to their unique properties [1-3]. Surface modification of metallic particles under wet ball milling in various organic media, including in the presence of surfactants [4], and in media whose composition is close to the composition of the dielectric polymer matrix is of great interest. Such milling results in the creation on the particles of thin surface layers, which play the role of an interface layer improving the adhesion of metallic particles to the polymer matrix and protect them from corrosion.

$Fe_{75}Si_{15}Al_{10}$ alloy was produced by ball milling of the elemental powder mixture in an argon atmosphere. Surface modification was carried out under wet ball milling in organosilicon block copolymer ("Lestosil SM") and surfactants (stearic and phenylanthranilic acids, sodium dodecyl sulfate) solutions, which are effective inhibitors of corrosion at the same time.

The produced materials were characterized by scanning electron microscopy, X-ray diffraction analysis and Mossbauer spectroscopy. The interaction of modifying agents with particles surface was evaluated by investigation of the surface layers of the particles after surface modification by X-ray photoelectron and IR spectroscopies. The corrosion behavior of the powders in aqueous solutions of 3 wt. % NaCl and 0.1 m. HCl was also investigated.

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# MECHANICALLY ALLOYED Ti-Nb ALLOYS FOR SELECTIVE LASER MELTING OF THE PRODUCTS FOR MEDICAL APPLICATIONS

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The mechanical alloying is the alternative method of the production of the metal powders applicable in the additive manufacturing. This method is not as expensive and complex as the traditional methods of the powders production for additive manufacturing, such as plasma, gas and centrifugal atomization. Mechanical alloying provides homogeneous mixture of the components, their interdiffusion and dissolution, which lead to the formation of the phase composition corresponding to the as-cast analogue. Produced with this method powders have wide range of particle distribution and near-spherical shape of the particles [1].

The aim is to produce Ti-(40-45) wt. % Nb alloy powder applicable for the selective laser melting with the mechanical alloying. The conditions of the formation of the alloys, the structure, phase composition and particle distribution of produced powders were evaluated. Mechanical alloying allows producing double-phased powders with the particle distribution applicable for the selective laser melting. The produced powder alloys were used for the selective laser melting of the Ti-(40-45) wt. % Nb alloy samples [2].

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# PHASE FORMATION IN MECHANICALLY ACTIVATED GAMMA-IRRADIATED Ti + Al MIXTURE DURING HIGH-TEMPERATURE SYNTHESIS BY INDUCTION HEATING

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The use of γ-irradiation of systems in a nonequilibrium state for realizing «fine» structure control is of particular interest. High-temperature synthesis was conducted under identical conditions in mechanically activated powder mixtures and mechanically activated γ-irradiated powder mixtures of the same Ti + Al composition. After reaching the maximum synthesis temperatures, the heating element was not disconnected; the process of rapid synthesis was continuously shifting to isothermal annealing process. The heating source was switched off at regular intervals.

When turning the system off immediately after the completed chemical reaction, the result of the synthesis in the activated mixtures is a multiphase product in a nonequilibrium state. The system stabilizes with increasing exposure. The same happens with 2 min annealing. The diffraction patterns show the prevailing reflections of TiAl and a small amount of metastable $Ti_3Al_5$ phase. The main TiAl phase decays with further increase of annealing time.

The X-ray diffraction patterns show that the multiphase product formed in the SHS of Ti + Al powder mixture preliminarily mechanically activated and then irradiated by γ-quanta. The result of the same synthesis followed by 2 min of annealing is a monophase TiAl intermetallic compound, the stabilization of system is observed. It should be noted that with an increase of annealing time up to 7 minutes, there is no decomposition of TiAl phase, as it was observed in the synthesis of mechanically activated Ti + Al mixtures without gamma irradiation exposure. Thus, the influence of gamma radiation on the initial mixture under certain conditions leads to the formation of a structurally homogeneous product of TiAl composition.

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# MECHANOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF Sr-SUBSTITUTED HYDROXYAPATITE

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Apatite is a member of the family of calcium orthophosphates. Compared with other calcium orthophosphates, it is more widely used in medicine [1]. In recent years, extensive research has been carried out on improving the properties of apatite by introducing substituents into its cation and anion sublattices [2]. It has been shown that partial replacement of calcium ions by strontium ions leads to an improvement in the mechanical strength of the apatite ceramics [2]. In addition, small strontium concentrations significantly stimulate the activity of osteoblasts and decrease the activity of osteoclasts.

Results of investigation of Sr-substituted hydroxyapatites synthesized by a fast mechanochemical method will be presented. A set of apatites $Ca_{10-x}Sr_x(PO_4)_6(OH)_2$ with different strontium concentrations was synthesized in a planetary ball mill AGO-2. It was determined that all synthesized samples are single-phase nanosized apatite with an average crystallite size of 25 nm. The full-profile Rietveld method analysis has shown that the lattice parameters of apatite increase with increasing substituent concentration. The structural refinement revealed that strontium atoms occupy both CaI and CaII sites of the apatite structure and that the occupancy of O4 site by the oxygen atoms (position of oxygen of OH group) does not change, and, therefore, does not depend on the substituent concentration. A decrease in the intensity of the line corresponding to the OH group libration vibration in the FTIR spectrum is explained by a change in the OH group local environment. The structural refinement confirms this assumption.

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# MECHANOCHEMICAL PRECURSOR TREATMENT FOR THE SYNTHESIS OF OVERSTOICHIOMETRIC SPINELS IN THE Li-Mn-O AND Li-Mg-Mn-O SYSTEMS

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Overstoichiometric spinels of the Li-Mn-O and Li-Mg-Mn-O systems are of significant interest as cathode materials for lithium- and hybrid lithium-magnesium ion batteries and as catalysts for oxidative methane coupling process [1]. The most valuable advantages of these systems spinel-structure phases are properties stability, availability of high-purity starting materials, environmental safety and the possibility of properties modification through the usage of solid solutions. Traditional «ceramic» methods of these spinels synthesis have significant limitations in the amount of inserted overstoichiometric Li and Mg [1]. The methods based on the intercalation of lithium and magnesium into a matrix with a spinel structure can serve as good alternative. Unfortunately, up-to-date intercalation methods are low-tech and cannot provide the synthesis of pure, homogenous products with desired composition and reproducible properties. These disadvantages are strictly determined by a chemical nature of applied intercalating agents [1]. Thus, the search for alternative intercalating agents is an actual problem of chemistry and material science. We review our studies on the methods for homogeneous overstoichiometric spinels of the Li-Mn-O and Li-Mg-Mn-O systems synthesis under mild conditions using LiH and $MgH_2$ as intercalating agents, as well as the role of precursors mechanochemical treatment for the synthesis. The advantages and comparative characteristics of the hydride intercalation method are considered from the viewpoint of chemical nature of hydrides as intercalating agents and formation of byproducts, as well as the stable and metastable phase equilibria arising during hydride intercalation process [2].

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# THE EFFECT OF MECHANOCHEMICAL ACTIVATION ON THE PHASE COMPOSITION, STRUCTURE AND CATALYTIC PROPERTIES OF $Sr_2TiO_4$

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Mix oxides with a structure of layered perovskite attract much attention due to physicochemical properties: superconductivity, great magnetoresistance, catalytic and photocatalytic activity. The most attractive method to synthesize strontium titanates ($Sr_{n+1}Ti_nO_{3n+1}$) is solid state reactions giving polycrystalline samples. The reaction time and temperature can be lowered by the application of activation techniques.

In this work we study the effect of mechanochemical activation (MA) of starting minerals ($TiO_2$ and $SrO/SrCO_3$) on phase and surface composition, texture, and catalytic properties of $Sr_2TiO_4$ in oxidative coupling of methane (OCM) at $850^oC$. All catalysts were prepared by mixing and intensive milling of stoichiometric amounts of starting compounds for 0-8 min in a planetary mill APF-5 with further calcinations at $1100^oC$ for 4 h. $Sr_2TiO_4$ catalyst prepared using co-precipitation (CP) method was used for comparison.

It was found that the duration of mechanochemical activation affects the phase composition and texture characteristics of the catalysts (specific surface area, total pore volume, size distribution) and catalytic activity in the OCM reaction as well. XRD investigations indicates the formation of a pure layered perovskite phase $Sr_2TiO_4$ only after activation of ($TiO_2$ + $SrCO_3$) mixture for 8 min. Mechanical treatment for 4 min results in multiphase composition including different Ruddlesden–Popper phases $Sr_{n+1}Ti_nO_{3n+1}$. The formation of $Sr_3Ti_2O_7$ and $SrTiO_3$ perovskites also was found after activation of ($TiO_2$ + SrO) mixture for 4-8 min. XPS analysis revealed the presence of perovskite layers $SrTiO_3$, which interchange with layers of strontium oxide on the surface of all MA catalysts. The $C_2$-yield in OCM reaction for these catalysts was measured to be 8-12% depending on the surface properties of the catalysts. In comparison, the CP catalyst has a lower specific surface, a significant enrichment of the strontium surface compounds results in a low methane conversion providing only 5% of the C2 yield in the OCM reaction. Method of (MA) in comparison with the method of (CP) is environmentally friendly and resource-saving.

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# SYNTHESIS AND CATALYTIC PROPERTIES OF BULK MOLYBDENUM SULFIDE CATALYSTS PREPARED BY MECHANICAL MILLING MOLYBDENITE IN THE PRESENCE OF SMALL AMOUNTS OF LIQUIDS

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In the field of modern technologies, there is a clear tendency towards a preference for methods of obtaining catalysts without the use of aqueous reagent solutions. In this paper, by the method of mechanoactivation (MA) of molybdenite, bulk (without carrier) sulphide hydrotreating catalysts were obtained. The process of milling molybdenite, as a dimensional precursor, was carried out in a vertical vibratory mill in an inert atmosphere, in the presence of vapors of small quantities of polar and nonpolar liquids, under conditions of predominance of shear strains over the shock. The inhibitory effect of methanol on the process of grinding large molybdenite crystals was found. The results of screening of the conditions of MA molybdenite providing samples with the most pronounced catalytic properties are given. Physicochemical characteristics of catalysts, particle sizes with their hydrodesulfurizing ability are discussed.

The presence of sulfate anions and S-O-containing structures on the surface of MA-molybdenite as products of the chemical degradation of metastable centers is proved. It has been shown that sulfate anions can screen the catalytic centers of the samples, keeping their activity at the initial level up to 6 months and providing at least 5-fold cyclic use in the model reaction. The benchmarks for the high activity of methanol-containing catalysts was founded: MA time equal to 8 hours; presence in the products of biphenyl in the amount of 40÷50%; pH value for aqueous catalyst suspensions of less than 2.1; preservation in the catalyst IR spectrum of a broad band at 916 $cm^{-1}$ after cyclic use.

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# EFFECTS OF HIGH-ENERGY BALL MILLING AND REACTIVE MILLING ON THE SYNTHESIS OF Mg-Co AND Mg-FeTi COMPOSITES AND Ti-Nb ALLOYS AND THEIR HYDROGEN STORAGE PROPERTIES

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$MgH_2$ is promising for hydrogen storage because of its considerably high hydrogen storage capacity (7.6 wt.%). However, some drawbacks concerning hydrogen storage properties limit its extensive usage. Among many approaches aimed to improve its H-storage properties, high energy ball milling, and reactive milling in hydrogen atmosphere are the most used. Regarding Mg-based materials, Mg mixed with transition metals can form complex hydrides, which are of much interest for hydrogen storage because of their high volumetric capacity. β-(Ti, Nb) alloys are potential for hydrogen storage because they are bcc solid solution alloys. Intermetallic compounds of transition metals are useful catalysts for hydrogen absorption/desorption in Mg. Among intermetallics compounds, TiFe is a good candidate because it absorbs and desorbs hydrogen at or near room temperature. This work presents H-properties of mixtures of XMg-Co (X = 2, 3, and 7), β titanium alloys (Ti/Nb atomic ratios of 1.0, 1.5, and 2.3), and the combination of nanostructured Mg with 40 wt.% TiFe. Such mixtures and alloys were prepared by reactive milling under a hydrogen atmosphere and/or high energy ball milling. Structural features and hydrogen storage properties were analyzed by different techniques: electron microscopy, in-situ synchrotron X-ray diffraction and thermal analysis techniques. Results showed that 2Mg-Co only formed the $Mg_2CoH_5$ complex hydride, while other stoichiometries formed different contents of $Mg_2CoH_5$ and $MgH_2$. $Mg_2CoH_5$ proved to be beneficial on the first H-desorption of MgH2. Ti/Nb atomic ratios in Ti-Nb alloys had a significant influence on lattice parameters, crystallite and particle sizes, kinetics, storage capacities, reversibility and desorption temperatures. H-properties in Mg-TiFe mixtures were significantly influenced by the kind of surface between Mg and TiFe, interfaces, particles' refinement, the spatial distribution of refined TiFe in the Mg matrix, the presence of free Fe and process of thermal activation.

# STRUCTURE OF MIXING ZONES AT THE ITERFACE OF EXPLOSIVELY WELDED MATERIALS

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Explosive welding is known as one of the most common techniques for joining dissimilar materials. During the welding the flyer plate accelerated by rapidly expanding detonation products experiences an oblique impact with nonmoving parent plate. Under specific conditions (collision angle and collision velocity) a strong metallurgical bond may appear at the interface. The properties of this bond mainly depend on structure of thin layers near the interface. Many researchers observed formation of wavy interfaces and specific mixing zones which appeared between the plates due to the high velocity collision. In this study the mechanism of waves and mixing zones formation is discussed. The instability of the interface and the turbulent motion in the mixing zones were reproduced using SPH numerical simulation. A novel mechanism of vortexes formation is proposed. The strain, strain rates, temperatures and cooling rates were estimated using various numerical simulation techniques.

The structure of the interfaces was studied using optical microscopy, scanning electron microscopy and transmission electron microscopy. Due to the mixing of materials at the interfaces and subsequent rapid solidification various metastable phases are formed in explosively welded materials. Depending on materials composition the mixing zones may have glassy, quasicrystalline or metastable crystalline structures. Due to the high cooling rates a lot of similarities between the rapid solidification techniques and explosive welding may arise.

Various applications of explosive welding are discussed. A particular attention is payed to fabrication of multilayer composites. Due to the specific structure of interfaces these composites possess enhanced fatigue properties and impact toughness.

This study was supported by Russian Science Foundation (project 17-72-10226).

# INTERACTION OF TITANIUM WITH MULTI-WALLED CARBON NANOTUBES DURING BALL MILLING, HEAT TREATMENT AND SPARK PLASMA SINTERING

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The focus of this study is the interaction between multi-walled carbon nanotubes (MWCNTs) and titanium during high-energy ball milling, thermal explosion ignited in the ball-milled mixtures and Spark Plasma Sintering. Phase and structural transformations occurring during ball milling of the Ti-4wt.%MWCNT mixture and subsequent heating/sintering were analyzed. The ball-milled powders contained nanostructured titanium, nanotube fragments, amorphous carbon and nano-sized carbon-deficient titanium carbide $TiC_x$. Upon heating, thermal explosion was observed in Ti-4wt.%MWCNT mixtures milled for 1.5-7 min. Shorter milling times were not sufficient for establishing proper interfacial contact, while longer milling time lead to the extensive formation of titanium carbide $TiC_x$, which lowers a possible heat release by the mixture upon ignition. Both the ignition temperature of Ti-4wt.%MWCNT and the maximum temperature developed during thermal explosion decrease with the milling time of the mixture. The structural characteristics, phase composition and mechanical properties of bulk materials Spark Plasma Sintered from the ball-milled the Ti-4wt.%MWCNT powder mixtures will be reported in this presentation.

This study is conducted within the state assignment to ISSCM SB RAS (project 0301-2018-0001).

# MORPHOLOGICAL AND PHASE CHANGES DURING SPARK PLASMA SINTERING OF MECHANICALLY MILLED METAL-CARBON MIXTURES

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Porous carbon materials and metal-carbon composites are important for a wide range of practical applications, such as lithium ion-batteries and supercapacitors. Metals of the iron subgroup are graphitization catalysts, and their presence in the composites determines the phase transformations of the carbon component during sintering of the powder mixtures.

In the present work, metal-carbon composites were prepared by mechanical milling of «metal-soot» powder mixtures followed by Spark Plasma Sintering (SPS). The main characteristic of SPS is pulsed current, which directly passes through the graphite die and powder compact. In the SPS, the heat generation is internal, in contrast to hot pressing, where the heat is provided by external heating elements. This allows achieving high heating rates (up to 1000 K/min), hence the sintering process generally is very fast (within a few minutes). This makes it possible to suppress grain growth and produce bulk nanostructured materials or coatings. Metals of iron subgroup (Ni, Fe, Co) were used as graphitization catalysts and space holders for the production of porous carbon materials. Porous carbon materials were obtained by selective dissolution of the metals from the sintered compacts in 10% aqueous solution of HCl.

The influence of the nature of metal catalyst and mechanical milling on the phase composition, microstructure and properties (specific surface area, porosity) of the obtained porous materials was investigated. The porous materials were investigated by XRD, SEM, TEM, specific surface area measurements and Raman spectroscopy. During the SPS, amorphous carbon transformed into graphite or participated in the formation of a carbide phase (in case of Fe), the transformations degree increasing with increasing sintering temperature. Porous graphitic materials with a specific surface area of 20-100 $m^2/g$ were obtained. It was shown that preliminary mechanical milling of metal-carbon mixtures is an efficient tool in tailoring the architecture and pore shape/size of porous graphitic materials obtained by selective dissolution of metals from sintered metal-carbon compacts.

# FABRICATION OF $NI_3AL$+B MATERIAL BY MECHANICAL ACTIVATION AND SPARK PLASMA SINTERING

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$Ni_3Al$ intermetallic is of particular interest due to anomalous dependence of its yield strength from the heating temperature. This phenomenon is advantageous from the point of application of the intermetallic compounds as a structural material in aircraft and rocket industry, chemical and power engineering. However, polycrystalline $Ni_3Al$ is brittle at the room temperature. One of the most efficient alloying elements is boron. In the recent years, heightened interest in the obtaining of materials based on intermetallic compounds produced by mechanical activation (MA) of powder mixtures and subsequent spark plasma sintering (SPS) has been aroused. The SPS technology allows producing high-strength materials with a low level of porosity and low residual stresses.

The aim of this paper was to investigate the structure and properties of bulk compacts formed by SPS of MA powder mixtures consisting of Ni, Al, B and the same powder mixtures without MA. Powder mixtures were prepared by two methods: mixing the initial powder composition and preliminary activation of the reaction mixtures in the AGO-2 planetary ball mill to give the compositions $Ni_{75}Al_{25}$ (at. %).

As a result, applying the processes of MA of powder mixture free from boron, and with boron addition and subsequent SPS allows obtaining a $Ni_3Al$ intermetallic compound. The provisional three-minute MA contributes to the formation of a homogeneous fine-grained structure of the material. The addition of small (0.1 wt. %) amount of boron to the initial mixture of nickel and aluminum improves the density of the sintered $Ni_3Al$ (98.8%). It leads to further increase in flexural bending strength, and maintaining corrosion resistance. This value (2200 MPa) is almost 3 times the bending strength of the sample of $Ni_3Al$ sintered without boron addition and almost 8 times higher than the strength of the intermetallic $Ni_3Al$ stoichiometric composition obtained by SPS without mechanical activation.

The reported study was funded by RFBR according to the research project № 18-33-00436.

# CATALYTIC CONVERSION OF MECHANICALLY ACTIVATED ASPEN WOOD TO LIQUID BIOFUELS IN SUPERCRITICAL ETHANOL

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Wood biomass is a promising renewable raw material for obtaining the valuable chemicals and liquid biofuels. The catalytic conversion of lignocellulosic biomass in supercritical ethanol allows to obtain the bio-liquids with a rather high yield. This presentation demonstrates the possibility to increase the yield of bio-liquids by the use of mechanical activation of the mixture wood – zeolite catalysts.

According to SEM data, the initial sample of aspen wood contains large, elongated particles with a size of more than 0.5 mm. The mechanical treatment of aspen wood–zeolite catalyst mixture in AGO-2 decreases the size of wood particles and changes their shape. In the mechanically treated wood, the destruction of such components as large vessels, fiber libris and tracheids was observed. In addition, this treatment contributes more homogenous distribution of catalyst particles in the mixture.

Mechanical treatment increases the conversion of wood, rises the yield of liquid and gaseous products and reduces the yield of solid residue. High-silica zeolite catalysts only slightly increase the conversion of wood at 270 °C. But they rise by 2.5 times the yield of liquid products, boiling below 180 °C and decrease the yield of solid residue.

Among the studied catalysts, the highest activity demonstrates the catalyst with a ratio Si/Al of 30, which has the highest concentration of acidic sites. In the presence of this catalyst, the conversion of aspen wood in supercritical ethanol at 270 °C reaches to 86.0 wt.% at ethanol pressure of 6.4 MPa and to 90 wt.% at 21.0 MPa. The yield of liquid products achieves to 83.5 wt.% at ethanol pressure of 6.4 MPa and 89.0 wt.% at pressure 21.0 MPa. Liquid products obtained at 270 °C are mainly represented by compounds, formed from wood polysaccharides: 5-HMF, furfural, levulinic acid, ethyl ester, propanoic ester, 2-hydroxy-ethyl ester. The solid residue of aspen wood catalytic conversion at 270 °C contains predominantly cellulose and lignin.

The reported study was supported by Russian Science Foundation, grant № 16-13-10326.

# SYNTHESIS OF POLYSACCHARIDES DERIVATIVES THROUGH SOLID-STATE REACTIVE EXTRUSION

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Modification of polymers by application of solid-state reactive co-extrusion to mixtures of polymers and organic reagents of different hydrophilicity is a promising way to new polymer materials. The most attractive feature of this method is that the entire modification process does not require melting of components and any solvents as reaction medium. Shear deformation provides numerous possibilities to circumvent many processing obstacles typical for preparation of polymeric materials under heterogeneous conditions.

Among the natural polymers one of the most widely used classes is polysaccharides. Non-toxicity, biocompatibility, as well as ability for biodegradation and abundance in nature make polysaccharides like cellulose, chitin and chitosan very promising objects for a variety of applications. Materials based on polysaccharides in the form of powders, granules, gels and films can be used as flocculants and sorbents for organic contaminants, heavy metals, etc.

The design of new efficient and ecologically safe processes for syntheses of polysaccharides with hydrophobic moieties is one of the main purposes of our current studies. Berstorff ZE-40 twin-screw extruder with a variable set of processing elements was employed. Productivity of solid-state processes: 5…20 kg/h; zone temperatures range: -5…300 °C; screw rotation speed: 10…500 rpm.

Of particular interest are the allyl-substituted chitosan derivatives prepared through reactive co-extrusion of chitosan powder with allyl bromide. Structure and composition of the products were evaluated by FTIR and NMR spectroscopy and confirmed by chemical analysis data. Total content of the allyl substitutes from 5 to 50 per 100 chitosan units as a function of component ratio in the reactive mixtures was revealed for the samples. Carrying out of the reaction without any additives leads to formation of N-alkylated derivatives selectively, whereas in the presence of NaOH the unsaturated ethers of chitosan are formed mainly. The obtained unsaturated derivatives can be used as components of photosensitive compositions for fabrication of three-dimensional biocompatible structures with well-defined architectonics using a laser microstereolithography.

# MECHANOCHEMICAL WASTE-TO-MATERIALS APPROACH FOR HALOGEN RECOVERY FROM HALOGENATED POLLUTANTS

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Obsolete halogenated chemicals such as pesticides, technical fluids, flame retardants, etc., banned from utilization because of their hazardousness, are often poorly stockpiled in huge amounts in developing countries, demanding for adequate disposal. High energy ball milling with cheap reagents (e.g. CaO, $SiO_2$, and Fe), used in large excess, was demonstrated to effectively achieve safe mineralization of such persistent organic pollutants. Nevertheless, such methodology produces large volume of milled residue, mainly constituted of unreacted reagent. An alternative Waste-to-Materials approach is proposed to achieve by mechanochemical reaction not only the halogenated organic pollutant mineralization, but also the stoichiometric generation of an almost pure product of industrial interest. Specifically, $La_2O_3$ is co-milled with brominated or perfluorinated obsolete chemicals in stoichiometric amounts, i.e. La:X=1 (X=F, Br), thus obtaining lanthanum oxyhalides (LaOX) as almost pure product, which are notable materials with unique luminescent, catalytic, and electric properties. During the reaction, $La_2O_3$ is firstly activated by ball milling, inducing charge transfer to the haloorganics and provoking halides release. Solid state reaction under ball milling between $La_2O_3$ and DPPH$^\bullet$ (a stable radical) confirms electron generation due to oxide vacancy accumulation. This phenomenon is responsible for pollutant carbon structure disproportionation into carbonate and amorphous carbon. Then, halides are dissolved into the oxide lattice to form the oxyhalide (Fig. 1 shows the reaction trend with perfluorooctane sulfonate [PFOS]). Mild calcination (T≈ 300°C) removes carbonaceous by-products, obtaining a >95%$_w$ LaOX.

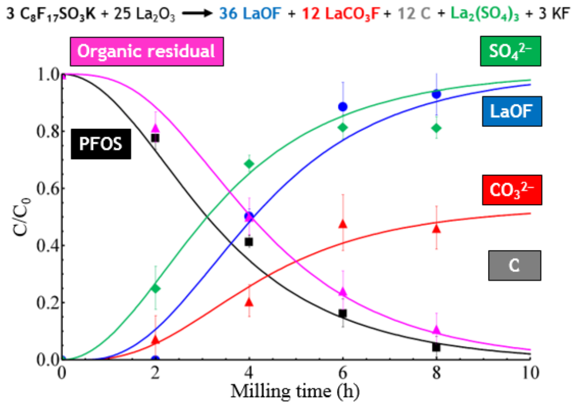

**Fig.1. PFOS + $La_2O_3$ mechanochemical reaction.**

# COMPARISON OF MICRONIZATION OF MEDICINAL SUBSTANCES BY METHODS OF MECHANOCHEMISTRY AND SUPERCRITICAL FLUID TECHNOLOGIES

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Mechanical methods of processing of solid substances are used to obtain microparticles of the right size and shape. These methods are relatively easy to perform, but have a number of shortcomings. First of all, this is a large loss of substance during processing. At the mechanical grinding of a solid substance, the product contains particles with sharp edges and is characterized by a wide particle size distribution. A multistage treatment is necessary after grinding to select the fraction of the desired size and impart the desired shape to the particles. At these stages, losses of the target product occur. When machined on the surface of solid substances can accumulate electrostatic charge. This not only leads to additional losses during packing due to poor flowability of the material, but also can negatively affect to the aerodynamic characteristics of the product.

Alternatively, the supercritical AntisSolvent precipitation (SAS) method can be used to solve this problem. The SAS method has a great number of opportunities to control over the size and morphology of the resulting microparticles. The number of parameters of the SAS process is large, and many of them are complexly dependent on each other.

The effect of antisolvent pressure, solution flow rate and salbutamol concentration in solution on the size and morphology of the particles produced were studied.

By varying the various parameters of the SAS process, it is possible to obtain salbutamol particles from 0.7 μm to 8.5 μm of needle-like, spherical, or close to it morphology, including particles that satisfy the size and morphology requirements for inhalation forms of the preparations.

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# SOLID-STATE MODIFIED CHITOSAN FOR REGENERATIVE MEDICINE

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Chitosan, a deacetylated derivative of naturally occurring polysaccharide chitin, possess a number of properties, which are desired for application in regenerative medicine, such as biodegradability, high biocompatibility due to a presence of specific macromolecular features. Further modification of chitosan chemical structure is a powerful tool to precisely control its biodegradation rate, hydrophilic-hydrophobic balance, mechanical characteristics, and biocompatibility to various cell lines as well as to extend a range of technologies, which could be applied to form based on scaffolds with well-defined 3D architectonics. In a frame of this presentation, a range of derivatives and graft-copolymers of chitosan synthetized through solid-state reactive blending will be discussed in terms of their applicability to fabricate biocompatible 3D scaffolds with tailored properties for tissue engineering. Substitution of chitosan amino groups by various ligands could be successfully used to prepare macroporous hydrogels with well-controlled biodegradation rate and biocompatibility via freeze-drying technique [1] or to fabricate hydrogels with tailored 3D architectonics via additive technologies [2, 3]. Grafting of oligo/polylactide fragments onto chitosan allows us to regulate macromolecules hydrophilic-hydrophobic balance and, thus, to use them for fabrication of microparticles with controlled surface/bulk morphology and chemistry [4] for future application as cell microcarriers or raw material for selective laser sintering as well as to use these graft-copolymers as biocompatible base of photosensitive composition for two-photon laser stereolithography [5].

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# PROCESSING IMAGES OBTAINED BY THE TRANSMISSION ELECTRON MICROSCOPY

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The work is carried out in order to fulfill the Agreement No.16-13-10200 between the Russian Science Foundation and Institute of Solid State Chemistry and Mechanochemistry SB RAS. The project is called "Controlled change in the structure and composition of plant raw materials by mechanochemical methods for intensifying the extraction of biologically active compounds".

Investigations are focused on a creation of scientific and technical solutions in the field of processing images of a textural type. The ultimate goal of the work is the determination of porosity, chemical reactivity, and other parameters.

Various sets of textural signs (about 20 features) and spectral transformations on the basis of orthogonal matrixes (6 transformations represent the greatest interest) is used for this purpose. Also experiments on application of the R/S-analysis and fractal analysis are carried out. Further for definition of a chemical reactivity, etc., it will be possible to use algorithms of machine teaching. For example, having trained system on a data set, it will be possible to carry out predictions concerning chemical properties.

The software products allowing us in details to analyze textures can be applied successfully in various areas of a science and the industry. First of all, it is the chemistry and materials technology. It is possible to analyze materials of an organic origin, cuts of metals and minerals, ceramics.

# ACCELERATED DECOMPOSITION OF DIOSCOREA SAPONIN BY MECHANICAL ACTIVATION

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An accelerated decomposition of dioscorea saponin isolated from the rhizome of *Dioscorea nipponica Makino* has been investigated by Size Analyzer, SEM, XRD, TG-DTA, and FTIR. The results showed that the granularity and structures are significantly different between the samples with and without mechanical activations.

Firstly, the sizes of D50 for the samples after activation by AGO mill have obviously decreased to as lower as 11.43 μ mas shown in Fig.1. Secondly, the crystalline saponin was significantly converted to amorphous one after activation as shown in XRD patterns of Fig.2.

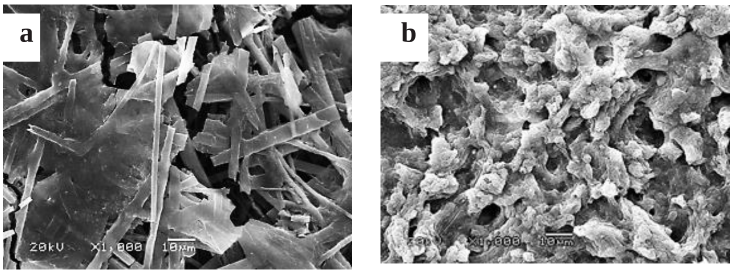

Fig.1 a) Saponin samples without activation; b) Saponin samples with activation.

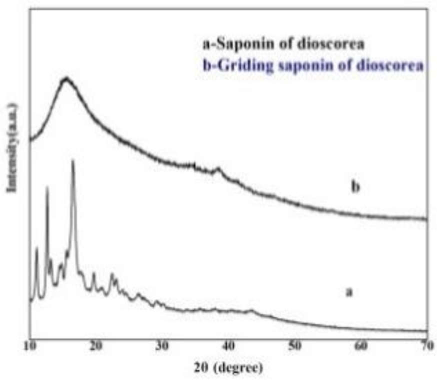

Fig.2 The XRD patterns before and after activation.

Finally, TG-DTA results have shown that the weight loss of the samples after activation has changed from two stages into one stage, and 99% weight loss has happened before 480 C as shown in Fig.3. It implied that decomposition of the saponin has been significantly accelerated due to additional energy accumulated inside the samples in a result of mechanical activation.

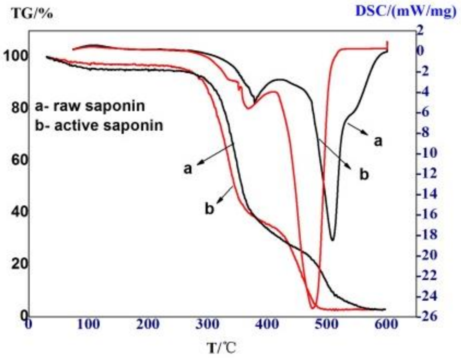

Fig.3

# OBTAINING AND PROPERTIES OF THE INNOVATIVE PREPARATION FOR TREATING FASCIOLIASIS

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It is known that fascioliasis is one of the most widespread and dangerous parasitic diseases of animals and humans. It is widely distributed not only in our country, but all over the world. The disease proceeds mainly chronically, and there is also an acute form with a severe clinical course, often with a case, resulting in significant economic damage to livestock. According to long-term observations, the slaughter yield of beef in animals affected by fascioliasis is 3.28% lower on average than in healthy animals, with the loss of 1000 heads of diseased bovine animals, an average of 495 kg of meat is lost. For dehelminthization of animals with fascioliasis, triclabendazole (TCB) is effective both against young and adult fasciolae. The disadvantage of the TCB-substance is its low solubility in water, which leads to a number of problems associated with waiting time and soil contamination with feces containing TCB. In order to increase the solubility of TCB, and therefore, the change in its bioavailability and pharmacokinetic properties, we used an innovative technology for the modification of TCB by its mechanochemical modification with arabinogalactan. The process of obtaining a composition of TCB:AG=1:10 was carried out in a roller ball mill with the realization of shock-abrasive type. The resulting solid dispersion (SD) of the preparation, which we have named "Triclafascide", is a finely dispersed, easily flowing powder with a maximum particle size of up to 10 microns. An analysis of the physicochemical and technological parameters of the preparation made it possible to speak of an increase in solubility by more than 8 times, which affected its activity against fasciolae. Namely, in clinical trials of the preparation in cattle at a dose of 2.5 mg/kg when administered individually orally in the form of an aqueous suspension and at a dose of 3.0 mg/kg in a mixture with food, it had 100% efficiency against fasciolae, i.e. in 5 times reduced therapeutic dose. Preclinical studies of triclafascide showed that the drug for acute toxicity, acute cutaneous toxicity refers to the 4-th class of low-toxic substances (according to GOST 12.1.007-76). Thus, using the mechanochemical technology of the modification of TCB with the help of the natural delivery means - arabinogalactan from the Siberian larch of Larix sibirica - we developed an original preparation for the treatment of fascioliasis of cattle.

# A NEW APPROACH IN THE DEVELOPMENT OF COMPLEX PREPARATIONS BASED ON BENZIMIDAZOLE DERIVATIVES FOR THE PROTECTION OF PLANTS

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It was discussed the results of studies on the development of formulations and original preparative forms of protectants based on benzimidazole substances (Carbendazim, Benomyl) using alternative form-building components.

By the testing of protectants based on the fungicide Benomyl, it was shown that these preparations completely healed the inoculum from fungi *Bipolaris sorokiniana*, *Fusarium spp*. During the entire vegetation period, new protectans successfully controlled root rot with a decrease in the development index in the phase of 2 leaves - in 2.1-2.7, in tillering - 1.2-1.4 and in milk ripeness - 1.4-1.5 times . These products studied influenced the growth processes and the density of crops, their positive impact was noted for almost all indicators of the structure of the productivity of soft spring wheat, which ultimately affected the yield of grain. The obtained results testify to the prospects of continuation of studies on optimization of preparative forms of protectants using mechanochemical methods.

Methods of mechanochemistry were used to obtain innovative compositions of fungicide-etchants based on Carbendazim and water-soluble polymers for complex protection of potatoes from pathogens during storage and black scab. It has been established that the introduction of arabinogalactan and hydroxyethyl starch polysaccharides into these preparations made it possible to significantly increase the water solubility of Carbendazim and to obtain potato tuber pickles with improved physico-chemical, technological and biological parameters. Testing protectants in the field showed synergy of biological properties, manifested in accelerating the growth of plants and their mass, reducing the development of black scab on stems and increasing the productivity of the crop. It was shown that the Carbendazim compositions with these polymers possessed high biological activity at a reduced consumption of the preparation.

# MECHANOCHEMICAL PREPARATION OF REMEDY FOR PROTECTION OF GRAIN CROPS WITH INCREASED EFFICIENCY

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It is known that from 30 to 60 % of all diseases in agricultural crops is transferred through the seeds and the soil. Treatment of seed is one of the most eco-friendly ways of use of chemicals. For innovative integrated seed treatments, the mechanochemical method of obtaining molecular complexes of well known fungicide agent tebuconazole (TBK) was used.

They consist from supramolecular complexes which form from natural organic substances, such as polysaccharide arabinogalactan and derivatives of natural saponin – glycyrrhizic acid. The dry compositions were prepared by milling in ball mill and include molecules of TBC as active drug. They were studied in solid phase and in solution by various physico - chemical methods. The formation of supramolecular structures and incorporation of TBC molecules into them were shown by increasing of intrinsic solubility of TBC, studying of solubility phase diagrams and $^1$H NMR relaxation technique in solutions of the compositions. The transport of TBC from solutions through the artificial membrane (PAMPA assay) and to the seeds was studied. The improving of absorption of TBK from its supramolecular systems has been shown. On the basis of the data, the optimal composition and conditions for the preparation of the compositions are justified. The obtained preparations were biologically tested in laboratory and field conditions and had shown high biological effectiveness against pathogenic micro flora in the treatment of spring wheat and barley seeds, the absence of a retardant effect and a positive impact on the productivity of these crops. The complex biological data, a composition superior to the widely used commercial drug RAXIL and reduce the flow rate/dose of FA to ~2 times were obtained.

# WATER SOLUBILITY ENHANCEMENT OF PINOSTROBIN OXIME BY MECHANOCHEMICAL TREATMENT

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Eleven flavonoid compounds [1] have been isolated from *Populusbalsamifera* L. gemma, particularly pinostrobin which has antiproliferative, neuroprotective, and anti-inflammatory properties [2]. A new high-potential compound pinostrobin oxime (PO) with hepatoprotective and antioxidant properties has been obtained by the reaction of pinostrobin with hydroxylamine hydrochloride. A major disadvantage of flavonoid substances is their poor water solubility which affects the bioavailability. Thus, it has become an urgent task to enhance the water solubility of PO.

This task was carried out by forming supramolecular structures of PO by mechanochemical treatment in a ball mill. We used a good water soluble polysaccharide arabinogalactan (AG), isolated from *Larix dahurica*, and a natural saponin derivative disodium salt of glycyrrhizic acid ($Na_2GA$) as complexing agents. Structural features of complexing agents promote formation of supramolecular complexes with processing matter, which molecules are bound by hydrogen bonds in the space formed by complexing agents’ macromolecules. $MgCO_3$ was also used to shift pH of PO solid dispersions to a slightly alkaline range, which also increased the water solubility. PO concentration in aqueous solutions of the obtained samples was determined by HPLC. As a result, 16-hour mill processing enhanced the water solubility of PO in complex with $Na_2GA$ by 300 times and with AG by 30 times. Whereas, 4-hour mill processing enhanced the water solubility of PO with $MgCO_3$ by 70 times.

Thus, we have achieved a significant increase of PO water solubility by mechanochemical treatment with complexing agents in a ball mill. The structure of PO molecules and, consequently, its biological properties have been preserved.

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# SEARCHING FOR 2- AND 4-HYDROXYBENZAMIDE COCRYSTALS POLYMORPHIC FORMS BY MECHANOCHEMICAL METHOD

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Polymorphism is of interest in crystallization, phase transition, materials synthesis, and the pharmaceutical industry because differences in the crystal packing and/or conformation of compounds with the same formula can change the chemical and physical properties, including solubility and bioavailability. Generally, polymorphic structures can be divided into two main categories, i.e., packing and conformational polymorphs. The conformational polymorphism is associated with molecules that contain one or more flexible fragments with relatively low energy barrier for rotation around covalent bonds. Packing polymorphism mainly occurs for conformationally rigid molecules which have a large energy penalty for conformational change. However, for the most of polymorphic systems the distinction between packing and conformational polymorphism is not obvious, since both types of changes (i.e., conformation and packing) are usually observed during polymorphic transition.

In the case of cocrystals, the difference between polymorphism types is even more unclear. Polymorphic forms of a cocrystal can be classified as packing polymorphs if the following conditions are fulfilled: (i) both polymorphs should be constructed from the components with minor differences in their conformations, (ii) both polymorphs should be sustained by the same synthons of hydrogen bonds. Obviously, simultaneous realization of these two conditions seems unlikely. Thus, descriptions of packing polymorphism for cocrystals are limited by only few examples.

In this work, we report the results of the experimental search for polymorphic forms of cocrystals of salicylamide and 4-hydroxybenzamide with dicarboxylic acids (oxalic and maleic acids) by various methods include solvent-drop grinding, slurry sonication technique, and crystallization procedure. Characterization of cocrystal polymorphs was carried out by powder X-ray diffraction, differential scanning calorimetry and thermogravimetric analysis. According to the results of the study, optimal conditions for the cocrystals polymorphic forms preparation were proposed.

This work was supported by the Russian Science Foundation (№ 17-73-10351).

# THE USE OF MECHANICALLY ACTIVATED LITHIUM CARBONATE TO INDUCE CANCER CELL DEATH

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One of the actual problems of modern science is the problem of induction of a cancer cell death. Lithium compounds considered as potential agents for targeted therapy that can affect on tumor growth. It is known that lithium carbonate inhibits the cancer cells proliferation due to the cycle arrest in $G_2$/M, induces apoptosis and modulates autophagy in cancer cells. However lithium toxicity limits its application for cancer therapy. On the other hand, the development of nanotechnologies reveals new characteristics of nanosized structures, more manifest in comparison with the initial forms. Therefore we studied biological effects of mechanically activated nanosized form of lithium carbonate ($Li_2CO_3$) in comparison with its initial form.

Hepatocellular carcinoma (HCC) is one of the aggressive cancer, resistant to drug therapy. Discovery of effective inducers of HCC cell death is very actual for HCC therapy. Using MTT test, the HCC cells viability was determined and a dose-dependent decrease in the viability of the cells exposed to $Li_2CO_3$ and mechanically activated nanosized form of $Li_2CO_3$ were revealed. Mechanical activation of $Li_2CO_3$ was performed in an AGO-2S planetary activator at 40g in air for 10 min. It has been shown that HCC cells are most susceptible to the damage effects of mechanically activated nanosized form of $Li_2CO_3$. By light, electron microscopy and flow cytometry it was shown that mechanically activated nanosized form of $Li_2CO_3$ induced apoptosis and autophagic death of HCC cells. We found that mechanically activated nanosized form of $Li_2CO_3$ in doses less than initial form was more effective for HCC cells. The possible mechanism of biological effect of activated $Li_2CO_3$ is discussed.

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# MECHANOSYNTHESIS OF TiC(NbC) – Cu COMPOSITES USING LIQUID HYDROCARBONS

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It is known that Ti, Zr, Nb, Fe, Cr carbides can be synthesized by milling of its powder in the presence of liquid hydrocarbons (toluene, heptane, oil, and so on) [1-3]. This method is expected to be used for obtaining the transition metal carbides/carbohydrides - based composite materials with extremely refined grain size, uniform distribution of the phases and the advanced properties.

Niobium carbide – 10 vol.% copper and titanium carbohydrides – 20-45 vol.% intermetallic phase (CuTi, $CuTi_2$) composites were obtained with the use of mechanosynthesis in liquid hydrocarbon (petroleum ether, xylene), followed by magnetic pulse compaction. The morphology, structural-phase composition, density, hardness and wear resistance of the composites were investigated.

This work was performed within the framework of the State Assignment of the Russian Federal Agency of Scientific Organizations (Number of State Registration of the Scientific Research AAAA-A17-117022250038-7), and partially supported by the Presidium of the Ural Branch of the Russian Academy of Science (project № 18-10-2-21).

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# ORGANIC SYNTHESIS BY MECHANOCHEMISTRY

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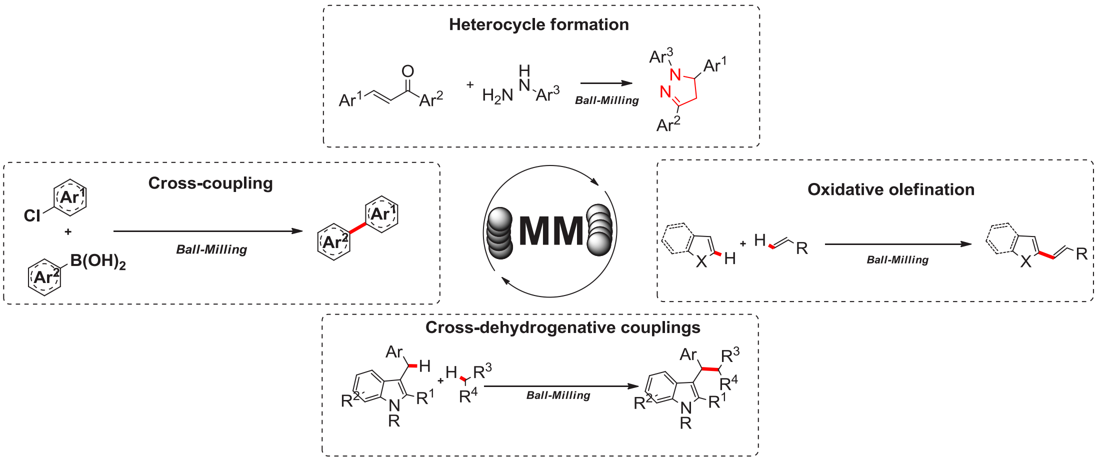

During the past century, the development of chemistry had enhanced significant influence on earth environment, which had counteracted on the human's living.

In the field of organic chemistry, the toxic solvent was one of the most important source of environmental pollution, and to overcome this problem a plenty of effort had been undertaken including solvent-free technologies and green solvents. Mechanochemical technique promoting solid state reactions had became one of the most powerful solvent-free synthetic technique during the past decade, which had shown its prominent features including solubility ignoring, high efficiency, and special selectivity. Examples will be given on application of mechanochemistry to the organic synthesis including heterocycle synthesis, cross-couplings, cross-dehydrogenative couplings, and oxidative olefination, which had been transformed from the conventional solvent-based reactions to the high-efficient solvent-free reactions. Different approaches will be introduced to transfer the conventional solvent conditions to the mechanochemical processes. Examples of investigation of mechanochemical processes also will be presented in some cases explaining the underlying mechanism of the mechanochemical reaction's special features.

Selected publications: (1) Green Chem. 11 (2009) 163; (2) J. Org. Chem. 76 (2011) 9144; (3) Tetrahedron Lett. 54 (2013) 2006; (4) RSC Adv. 4 (2014) 22775; (5) Green Chem. 17 (2015) 2330; (6) J. Org. Chem. 81 (2016) 6049; (7) J. Org. Chem. 81 (2016) 10049; (8) J. Org. Chem. (2016) 11514.

# MECHANOCHEMICAL PREPARATION OF SUPRAMOLECULE'S DELIVERY SYSTEMS FOR BIOLOGY ACTIVE MOLECULES

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The newest results of application areas and advantages of mechanochemical technology of drug modification are considered. The main approach for pharmacy is based on preparation of solid disperse systems of pharmaceutics' substances with different auxiliaries – oligo- and polysaccharide, plant's saponins, synthetic polymers, amorphous silica substances. After dissolution in water they form inclusion complexes, micelles and nanoparticles, which containing drug molecules. Noted processes provide sufficiently increasing of solubility, bioavailability and pharmacology action (lowering of meaning doses in 2-100 folds) of drug. There is briefly discussion the various designs of mill for mechanochemistry and recommendations for their use [1-6], for examples.

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# MECHANOCHEMICAL METHOD OF OBTAINING ANTHELMINTIC DRUGS WITH INCREASED ACTIVITY

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Helminthiases are among the most dangerous parasitic diseases of humans, animals and plants, and therefore the development of effective anthelmintic drugs remains an urgent problem of modern science.

Known methods for the treatment of animal helminthiases are based on the use of a wide range of anthelmintic drugs, many of which, due to their poor solubility, often do not provide the necessary efficacy. To achieve desirable result, it is necessary to use overestimated dosages of drugs, which, in turn, leads to an increase in the likelihood of undesirable side effects.

To improve the solubility of anthelmintic drug substances, methods based on the formation of their intermolecular complexes with water-soluble synthetic and/or natural polymers are often used. Such an approach in many cases allows to achieve reduction of dosages of medicinal substances while maintaining therapeutic activity, as well as reducing their toxicity.

We propose an innovative approach to the creation of effective benzimidazole anthelmintic preparations by mechanochemical modification of their substances with water-soluble polymers in ball mills with shock-abrading type of action.

Our researches confirmed the possibility of solid-phase mechanochemical technology to increase the solubility of poorly soluble substances of medicinal substances by their joint treatment with water-soluble polymers in energy-controlled activators. The resulting preparations have not only increased solubility, but also high activity with reduced doses of the preparation. In this case, the drugs exhibit an extended spectrum of activity, not inherent in the original substance.

# STUDY OF PHARMACOLOGICAL ACTIVITY OF SUPRAMOLECULAR COMPLEXES OF DRUGS WITH PLANT METABOLITES OBTAINED BY MECHANOCHEMICAL METHOD

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To overcome limitations of oral drug delivery "host-guest" inclusion complexes of drugs with natural polysaccharide arabinogalactan (AG) and saponin glycyrrhizic acid (GA) can be applied. Most of the commercially available AG is obtained from woody tissue of larches, in Russia it is *Larix sibirica* and *gmelinii*. GA is the chief sweet-tasting constituent of *Glycyrrhiza glabra*. It is used worldwide as a food sweetener and as part of licorice preparations, as a medicinal product. All studied inclusion complexes were synthesized mechanochemically and characterized by water solubility, electron microscopy, differential scanning calorimetry, X-ray powder diffraction analysis and $^1$H-nuclear magnetic resonance spectroscopy. For all of them primary pharmacological properties were evaluated *in vivo*. For the several complexes pharmacokinetic parameters after oral introduction were obtained (Cmax, Tmax, AUC, $T_{1\backslash 2}$, MRT). We have studied AG and/or GA inclusion complexes with following drugs: NSAIDs aspirin, ibuprofen, naproxen; antihypertensive drug nifedipine; broad-spectrum antihelminthic agents albendazole and praziquantel; cholesterol lowering drugs simvastatin and atorvastatin. In all cases it was found that such complexation results in significant drug's bioavailability enhancement and effective dose reduction.

Thus, inclusion complexes with AG and GA are a simple and effective way to enhance oral bioavailability of different drugs.

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# MECHANOCHEMICAL MODIFICATION OF FLAVONOIDS BY OBTAINING SUPRAMOLECULAR COMPLEXES WITH POLYSACCHARIDE ARABINOGALACTAN AND GLYCYRRHIZIC ACID DISODIUM SALT FOR INCREASING THEIR SOLUBILITY AND MEMBRANE PERMEABILITY

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Currently, special attention is paid to the creation of effective medication that can reduce the damage from free radical processes in the body as well as aimed at the prevention and treatment of nutrition-related diseases. Examples of such drugs are the plant's flavonoids. They demonstrate a wide spectrum of activity in the human body: antioxidant activity, capillary protective, and reduce the risk of cardiovascular disease actions. On the other hand, extremely low water solubility and membrane permeability of flavonoids restricts their practical application as components of food or medicinal formulations.

To improve the water solubility and membrane permeability we used mechanochemical approach. Solid dispersions based on flavonoids (puerarin, genistein, rutin, dihydroquercetin) with water-soluble larch polysaccharide arabinogalactan (AG) [1] and disodium salt of glycyrrhizic acid ($Na_2GA$)were prepared.

Increasing of water solubility is achieved through the formation of “host-guest” complexes (with AG) and inclusion of molecules of flavonoids in the micelles (with $Na_2GA$) which are formed in aqueous solutions of $Na_2GA$ [2].

It was found that flavonoids solubility increases (in ~1,5-9 times) in all samples prepared by mechanochemical technique. These results are interesting for the development of improved dietary supplements and medicines.

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# MECHANOCHEMICAL SYNTHESIS OF SOLID COMPOSITIONS OF PRAZIQUANTEL AND ALBENDAZOLE FOR IMPROVEMENT OF THEIR ANTI-OPISTHORCHOSIS ACTION

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Obtaining of pharmaceutical solid dispersions is one of the techniques to solve the problems of low solubility and bioavailability of drug. Mechanochemical technology is known as a simple and “green” method to obtain solid dispersions. Besides, using this method one can obtain solid dispersions of hydrophobic drugs with hydrophilic carriers. Opisthorchosis caused by *Opisthorchis felineus* is a widespread disease in Russia, especially in Western Siberia. The drug of choice for opisthorchosis treatment (praziquantel) possess insufficient activity and shows side effects. Albendazole is a drug for treatment of intestinal helmenthiasis, which possess potential activity against opisthorchis. But due to its extremely low aqueous solubility and consequently its low bioavailability, albendazole is not used for opisthorchosis treatment. The purpose of this work was to obtain solid dispersions of these drugs with hydrophilic carriers – polysaccharide arabinogalactan extracted from larch wood and glycyrrhizic acid disodium salt which is a derivative of triterpene glycoside extracted from licorice root. The compositions were investigated in solid state and in solution using a variety of physicochemical methods. It was shown that solubility increases for all drugs under investigation. The supramolecular structures in solutions of solid dispersion were investigated using NMR-relaxation method. The increased anti-opisthorchosis efficacy of the obtained compositions was shown in the model of opisthorchosis in golden hamsters. Solid dispersions of praziquantel showed anti-opisthorchosis activity enhancement by a factor of 4-11.

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# EFFECT OF MECHANOCHEMICAL PROCESSING ON THE CELLULAR STRUCTURE AND EXTRACTION CHARACTERISTICS OF PLANT RAW MATERIALS

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The theory of diffusion extraction of porous solids has been developed by the mid-1970s. Its essence lies in the fact that the mass transfer of the target components in the porous particles is carried out exclusively as a result of molecular diffusion. There are few studies that have investigated the optimal grinding of raw materials and the transformation of its porous structure from the point of view of extraction processes. The review of modern achievements of mechanochemical processing of plant raw materials, control of particle dispersion, the ordering of the ultrastructure of cell walls is presented in [1, 2].

In our work, the influence of changes in the cellular structure of plant raw materials on extraction processes was investigated. It is shown that the diffusion coefficient through the cell wall increases with increasing degree of disordering. On the contrary, the diffusion coefficient in the pores decreases with disordering. Adding these effects leads to the fact that the dependence of the effective diffusion constant has a domed shape with a maximum in the region of the crystallinity index of 40-50%. The decrease in the diffusion constant for high disordering is explained by the "collapse" of the conducting channels. Based on the calculated effective diffusion coefficients, flows of the model substance (resveratrol) from 1 g of particles of a given size were calculated. For highly ordered particles (index of crystallinity - 65%), the flow of matter is practically independent of the particle size. For disordered particles the flow depends on the particle size. Reducing the particle size from 400 to 20 μm results in a 2-fold increase in the flow, while a change in the crystallinity index from 65 to an optimum 41% (for example, for particles of 200 μm) leads to increase in the flow by a factor of 3. In optimum conditions, it is possible to increase the flow of matter up to 18 times. Thus, it is shown that at mechanical treatment of plant raw materials, there are optimal parameters, determined not only by the size of the raw material, but also by the degree of disaggregation.

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# EFFECT OF LIGNOCELLULOSIC SUBSTRATE ON THE STABILITY OF CELLULOLYTIC ENZYMES DURING JOINT MECHANICAL TREATMENT

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In this work, the effect of lignocellulosic substrate on the denaturation of a cellulosolytic enzyme complex under joint mechanical treatment in ball and centrifugal roller type semi-industrial mills was studied.

It was shown [1] that during mechanical treatment of enzymes with a lignocellulosic substrate, two parallel processes are observed: denaturation of enzymes and activation of lignocellulose. At the same time, during the simultaneous processing of the lignocellulosic substrate and the enzymes, the stability of the enzymes to mechanical action is significantly increased in comparison with the mechanical treatment of enzyme preparations without a substrate.

To save the catalytic activity during treatment in the centrifugal roller mills-activator it is necessary to minimize the action time of the enzymes in the treatment zone while increasing the degree of filling of the apparatus.

It has been demonstrated that the sorption of the cellulosolytic complex from the solution on the surface of the plant raw material and the subsequent drying lead to stabilization of the enzymes. The subsequent mechanical activation at a high feed rate in to the treatment zone (a small specific dose of mechanical energy) preserves (but does not decrease) the reactivity of the sorbed enzymes at the same level.

A decreasing of the feed rate during mechanical activation causes an increase in the dose of energy supplied and an increase in reactivity of 30-40%, which can be explained by the distribution of the enzyme molecules along the pores and the surface layer of the disordered substrate.

Thus, choosing the conditions of mechanochemical treatment helps not only to prevent denaturation of enzymes, but, in some cases, to increase the rate of enzymatic hydrolysis.

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# CHEMICAL CONSTITUENT OF *GALEGA ORIENTALIS* WATER SOLUBLE SUBSTANCES PRODUCED BY MECHANOCHEMICAL PROCEDURE

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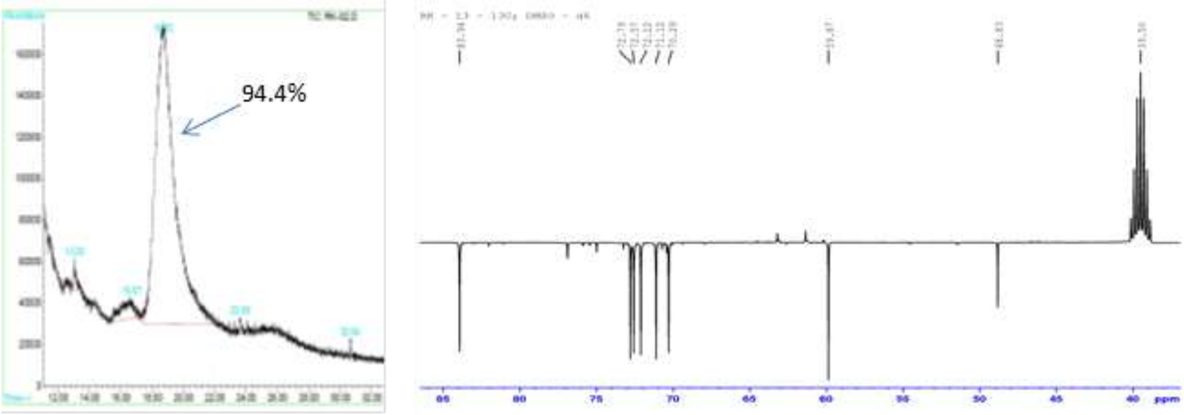
*Galega orientalis* Lam. is a species of flowering plant in the Fabaceae, the Legume family. Aqueous extract of *G. orientalis* revealed hypoglycemic activity as it was reported [1].

We have studied the chemical constituent of *G. orientalis* herb’s water-soluble substances (WSS). The plant material was mechanically activated followed by water extraction with Soxhlet apparatus. The yield of WSS was 31.1%. The chemical constituent of WSS was studied by the method of consecutive extraction of WSS water solution using solvents of different polarity. The extracts obtained were analyzed by GC/MS method. The dimethyl sulfoxide (DMSO) extract contained monomethyl inositol (94.4%). The monomethyl inositol structure was determined by spectral methods as. D-pinitole (3-O-methyl D-Chiro-inositol). The NMR 1H and 13C data coincide with those cited in the literature [2].



GC/MS profile and $^{13}$C NMR spectrum of D-pinitole.

D-pinitole has been reported to possess antidiabetic and hypoglycaemic activities [3].

[1] Osmanova N.A. et al., Some Pharmacological properties of above-ground part of Galega officinalis L. and G. orientalis Lam. Rastitelnye Resursy, 4 (2003) 119-129.
[2] Ismanova G.A. et al., Glucoside of taxifolin and (+)-pinitol from Pinus sylvestris. Chem. Nat. Comp., 49, 2 (2013) 345-346.
[3] Bates S.H. et al., Insulin-like effect of pinitol, British Journal of Pharmacology, 130 (2000) 1944-1948.

# MECHANOCHEMICAL EXTRACTION OF PSORALEA DRUPACEA SECONDARY METABOLITES

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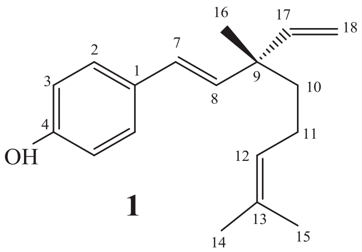
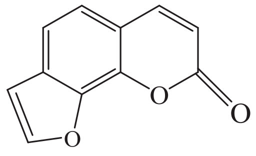
*Psoralea drupacea* Bunge (Fabaceae family) grows widely in Uzbekistan and Kazakhstan. Secondary metabolites isolated from *P. drupacea* possess a wide spectrum of biological activity. It is known the use of mechanochemical activation methods provides an increase in the yield of target product, reduction of the amount of solvents, time and energy costs to obtain the target products compared to conventional extraction processes. We have studied the chemical constituents of *P. drupacea* Bunge roots and seeds mechanically activated together with silica gel as well as alumina. Activated reaction mass was treated with appropriate solvents and analyzed via GC/MS method. It has been discovered that the main component of the seeds was bakuchiol (4-[(1E,3S)-3,7-dimethyl-3-vinyl-1,6-octadien-1-yl]phenol) (**1**). [1]. Moreover furocoumarins such as angelicin (**2**), psoralen (**3**) as well as monomehtyl inositol (**4**) were identified in the roots and seeds of *P. drupacea* using GC-MS method. The compounds **1** – **4** possess high biological activity [1-3].



**1**



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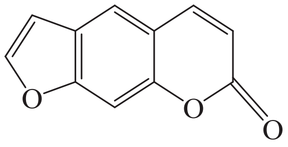

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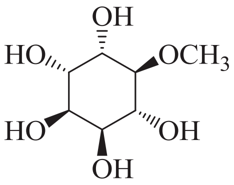

**4**

[1] Lystvan K., Belokurova V., Sheludko Y. et al., Plant Cell, Tissue and Organ Culture 101 (2010) 99–103.

[2] Sharique A. Ali et al. Pharmaceutical Biology 49(4) (2011) 422–427.

[3] Bates S.H. et al. British Journal of Pharmacology. 130 (2000) 1944-1948.

# MECHANOCHEMICAL SYNTHESIS OF ELEMENTORGANOSILOXANES

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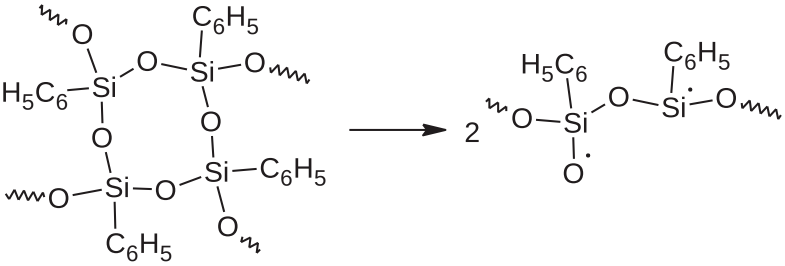
In the present work, the mechanochemical synthesis of elementorganosiloxanes containing atoms of magnesium, calcium, boron, aluminum, gallium and tin has been studied.

The matrix-activated lasers desorption/ionization method has shown that as a result of mechanochemical activation, the siloxane bond is broken in the initial polyphenylsilsesquioxane to form low molecular weight activated centers:



It has been established that when using acetylacetonates of alkaline earth metals, the heteroatom enters the siloxane chain, the better the larger the ionic radius of the metal. When acetylacetonates of p-elements were introduced in the reaction, an inverse regularity was observed.

It has been established that in the case of introduction of halogen derivatives of boron and tin as starting materials of acetylacetonates into the reaction, the humidity of the air significantly influences the course of the process, leading to increased hydrolysis of the initial derivatives during activation.

The influence of the functionality of the initial organosilicon derivative and organic derivatives of heteroatoms (on the example of boron compounds) is studied. It is shown that a decrease in the functionality of the organosilicon derivative leads to the formation of low molecular weight products, while a decrease in the functionality of the heteroatom derivative leads to the formation of products with a smaller ratio compared to a given Si/M ratio. The replacement of acetylacetonate with benzoylacetonate and dibenzoylmethanate results in a decrease in the reactivity of the organoboron compound.

# CORRELATION METHODS OF ANALYSIS IN STUDIES OF MECHANOCHEMICAL REACTIONS

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The possibility of using the method of two-dimensional correlation spectroscopy [1] for a step-by-step study of deformation-induced conversions and transformations of molecular crystals is shown in this work.

The physical and chemical mechanisms of mechanochemically induced conversions and transformations in the nanostructured low-symmetry molecular crystals are discussed.

As result of comprehensive research involving direct structural and structure-sensitive spectroscopic techniques, as well as quantum chemical simulations, the conditions necessary to obtain the polymorphic molecular compounds by mechanical activation were formulated, and the interrelation of the kinetics of their production with the amorphization and the formation of nano-dispersed states of molecular crystals (i.e., plane 2-D structures, nanotubes) was established.

The reported study was funded by RFBR according to the research project № 16-03-01131-a and partially by the FASO project № AAAA-A17-117022250038-7.

[1] Noda I., Ozaki Y. Two-Dimensional Correlation Spectroscopy, in: Applications in Vibrational and Optical Spectroscopy, Wiley: Chichester, UK, 2004.

# MECHANOCHEMICAL INTERACTION OF FLAVONOID QUERCETIN AND CARBOHYDRATE GLUCOSE. GLYCOSIDE BOND APPEARANCE BY IRS-DATA

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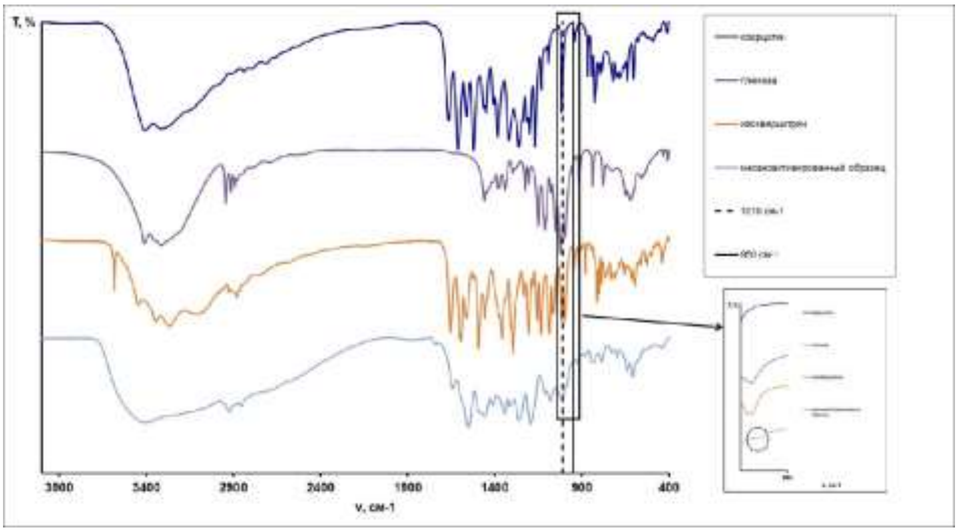
Flavonoids and their water soluble glycosides have perspective biological activity. Glycosides formation by reaction of polyphenol quercetin with carbohydrate glucose in solution is labour-consuming and very expensive. Mechanochemical activation of reaction mixture allows to simplify synthesis of glycosides and preparation of powders. The aim of this work is to show a possibility of mechanochemical activation for preparation of glycosides from quercetin and glucose and to confirm a glycoside-type bonds formation by IR-spectroscopic data.

In isoquercitrin, quercetin-3-β-D-glucopyranoside is shown as the preferable product in reaction of quercetin with glucose. Commercial reactants are chosen as the initial reagents and comparison samples: glucose, quercetin, isoquercitrin. Mixtures of powders of glucose and quercetin were treated in AGO-2 mill-activator, regime of 1 Wt/g. IR-spectra were simulated quantum chemically and measured experimentally on the Tensor 27 (Bruker) spectrometer, in potassium bromide.



Formation of glycoside type bonds leads to some specific absorption bands in IR spectrum. One may consider as a characteristic the range of 950-1050 $cm^{-1}$, which is responsible for complex vibrations (figure) of quercetin - glycoside bridge - glucopyranose cycle. New absorption bands in comparison with initial quercetin and glucose were shown. These bands are similar to ones of reference compound isoquercitrin. Existence of appeared vibration bands indicates formation of a glycoside in the mechanochemical synthesis.

The work is supported by RSF, grant No. 16-13-10200.

# MECHANOCHEMICAL MODIFICATION OF BROWN COAL HUMIC ACIDS FOR COMPLEX SORBENTS OF HEAVY METALS

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Brown coal is one of the most important industrial source of humic acids (HA). The common methods of extraction of HA from brown coal include the use of alkali, acids and organic solvents and are accompanied by high impact on environment [1]. However, some applications do not require extraction in the case of brown coal with high yield of HA. One of the ways to increase the yield of HS in brown coal and to modify their structure is to use a mechanochemical treatment [2].

The aim of this work was to investigate the impact of oxidative mechanochemical treatment (MT) of brown coal on its humic acids.

As a result of mechanochemical treatment with sodium percarbonate, the yeild of humic acids in brown coal was increased from 23,6% to 70%. The content of phenolic groups is increased by 55%, carboxyl - by 103%. The IR-spectra of humic acids before and after mechanochemical treatment of brown coal (Fig.1) demonstrates that there are complexes of metals with carboxyl groups, which are not removed during isolation of humic acids and their purification by cation exchanger. Mechanochemical treatment of brown coal with sodium percarbonate leads to the destruction of these complexes and the formation of new phenolic and carboxyl groups.

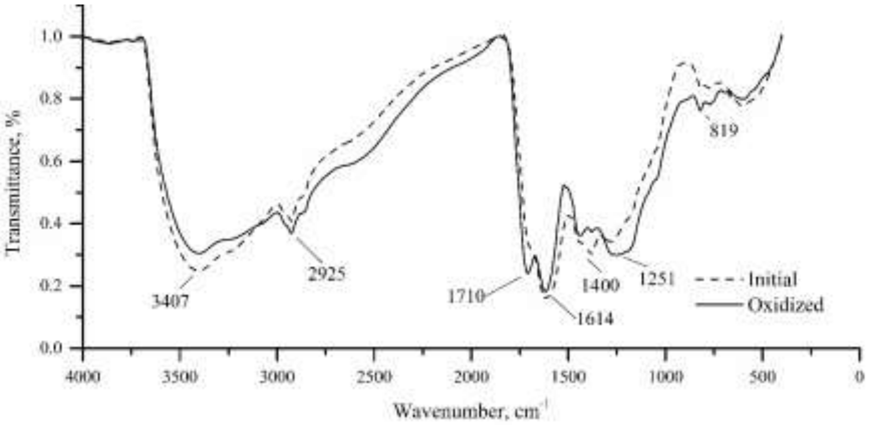

Fig. 1. IR spectra of humic acids isolated from brown coal before and after MT.

[1] Ivanov A.A., Savel'eva N.V. et al. Russ. J. Appl. Chem. 78(3) (2005) 506-510.

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# MECHANOCHEMISTRY FOR PRODUCING NANOCOMPOSITES BASED ON POLYETHYLENE AND POLYAMIDE

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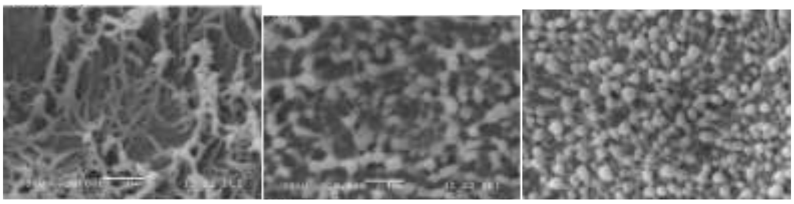
The mechanochemical method of producing powder composites from polymers and inorganic ultrafine particles with following fabrication of films based on them has been investigated. The powders of linear low density polyethylene "Exxon Mobile$^{TM}$LLDPE6101RQ" and polyamide "D 1894 A P 0-800 Griltex$^{®}$EMS" (hereinafter: PE and PA, respectively) were used as a polymer matrix; as an inorganic component – the nanopowders of $CaCO_3$, $SiO_2$, $TiO_2$, natural layered mineral Na-montmorillonite.

The mixture of polymer and inorganic powder was treated in the planetary-centrifugal activators for 20-60 seconds. Using the resulting composite, the films of thickness 40-500 μm were formed by different methods. It has been established that the composite crystallized in the form of volume grids with a certain size of crystallization cell.



(x 20000)

**Fig. 1. SEM of films based on PE: 1) 0.1% $SiO_2$; 2) 1% $TiO_2$ , 3) initial**

Fig. 1 presents the photomicrographs of films based on PE with the additives, mass %: 0.1 $SiO_2$, (1), 1% $TiO_2$ (2), without additives (3). As for the films based on PE containing inorganic additions of $TiO_2$, $CaCO_3$, $SiO_2$ or Na-montmorillonite in the amount of 0.01-5%, gas permeability is reduced up to 30-56%; the modulus of elasticity (along) increases up to 24-60%; strength characteristics are improved up to 15%. As for the films based on PA, containing inorganic additions of $TiO_2$ in the amount of 0.1-1%, gas permeability decreases by several tens of times (compared to the initial unmodified polyamide).

The mechanochemical method allows to more efficiently mix and uniformly distribute the hydrophilic inorganic particles in a hydrophobic matrix of polymers, to significantly speed up the process of dispersing (compared with the dispersion in the melt), not to apply additional dispersing agents, not to use solvents.

# INFLUENCE OF IR RADIATION AND MECHANICAL TREATMENT OF CEREAL GRAIN ON EFFICIENCY OF MECHANO-ENZYMATIC CONVERSION

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Sugary starch products in the form of various treacles are widely used in production of innovative feed additives and successfully replace traditional sugar in food industry. The actual industrial technologies of starch bioconversion into sugary starch products are complex multistage and energy-consuming processes. One of the reasons a low reactivity of starch results from its semi-crystalline structure that interferes availability of the biopolymers amylase and amylopectin for enzymes. It is necessary for passing of the enzymatic hydrolysis that amylase and amylopectin have passed into solution. For successful hydrolysis it is necessary to destroy crystal lamellas of native starch. At present, there are various physical and chemical methods used for destruction of starched granules. In particular we have used thermal and mechanical methods of starch grain activation. It was found that the largest concentration of carbohydrates in treacle resulting in enzymatic hydrolysis of starch before radiation was about 17% in 280 min. and then it stays constant. After radiation, the concentration of carbohydrates resulting in enzymatic hydrolysis of starch is reached 17% in 160 minutes and then increases following 280 minutes up to 26%. Specific energy consumption on hydrolysis of starches is 5.45 kW·h/kg for unirradiated starch and 4.04 kW·h/kg for the irradiated starch. In other words, energy consumption of hydrolysis of starch after IR radiation decreases in 1.75 times. In generally, one processes starch in colloidal state after its gelatinization. It has been shown that preliminary mechanical treatment of solid cereal grains and wheat starches significantly reduces their temperature of swelling and gelatinization. We have found conditions of starches treatment which provide its gelatinization in cool water and starched suspension at the room temperature shows rheological properties of polymeric solution.

# USE OF WASTE OF MECHANOCHEMICAL PROCESSING OF LIGNIN-CELLULOSE RAW MATERIAL FOR ENVIRONMENTALLY SAFE POWER ENGINEERING

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An integrated approach for the use of cellulose and lignin can be proposed to decentralized energy consumers that have cereal straw. In the straw of cereals, the ratio of cellulose and lignin components is about 50%:50%. The cellulose component can/must be used at the biochemical plants to produce bioethanol. The lignin component, which is a waste of biochemical productions, should be considered a promising type of renewable energy resources. Using this resource, it is possible to solve the problem of providing thermal energy for biochemical production, and in the case of surplus energy, it becomes possible to supply energy to the associated consumers.

An option for mechanochemical processing of 30,000 tones of straw per year at a biotechnology enterprise, potentially located in the Ordynsky district of the Novosibirsk region (a potential supplier of straw), was considered. In the biotechnological process, the maximal amount of straw processing waste by the developed technology is 24,000 t/y or 4 t/h; these processed wastes can be flared on a serial gas-oil boiler DE-10-14-GM with steam production of 10 tons of steam/h, converted for combustion of solid dispersed lignin-containing fuel. This requires the construction of a special boiler house. At the same time, thermal energy will be provided for a biotechnological enterprise and it will be possible to sell energy to associated consumers.

For the biotechnological enterprise, the construction of a boiler house on solid dispersed lignin-containing fuel can be considered an economically efficient project, taking into account the additional capital costs for boiler house construction and revenues generated by heat supply to the enterprise itself and sale of surplus thermal energy. The calculations showed that with the accepted initial data, the discounted payback period (the period of investment return) for 10 years of operation is about 1.5 years.

# STUDIES OF THE KINETICS OF THERMAL DECOMPOSITION AND COMBUSTION OF MECHANICALLY ACTIVATED MICROGRINDING COALS

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The technology of mechanically activated grinding, investigated in IT SB RAS, allows to exclude gas or fuel oil from the processes of ignition and combustion stabilization, this technology was tested on a large 5 MW fire stand. As a result of the experiments, it was found that mechanically activated carbon possesses increased chemical activity, ignites and burns with subsequent exiting to an autothermic regime, similar to gas-oil fuels [1].

The actual question is the reaction characteristics of the coals during mechanical activation grinding and the effect of the mechanical activation on the ignition and subsequent burning of coal. In this work, studies of the chemical activity of mechanically activated carbon are carried out using two different methods: the determination of the ignition temperature of coal dust in a vertical furnace tube and thermogravimetric analysis.

Experiments on a vertical tube furnace showed that the mechanically activated grinding temperature changes the ignition temperature of the coals, and according to the results of TGA it is noted that the activation energy of coal fuel depends on the method of its grinding and changes during its burning out.

Data are obtained on the increase in the chemical activity of coals according to the ignition temperature and the kinetic characteristics of the coals of various stages of metamorphism and the type of breakage.

The experiments showed a significant improvement in the quality of coal fuel that has undergone mechanical activation grinding, which makes it possible to effectively use it in the technology of substituting gas and fuel oil during ignition and stabilizing the combustion of a pulverized-coal torch in an energy boiler.

The study was carried out with the financial support of the Russian Foundation for Basic Research within the framework of the scientific project No. 18-38-00416.

[1] Burdukov A.P., Butakov E. B., Popov V.I., Chernetskiy M.Yu., Chernetskaya N.S. The use of mechanically activated micronized coal in thermal power engineering. Thermal Science. 20 (2016) 23–33.

# FABRICATION OF NANOMATERIALS AND THEIR POTENTIAL APPLICATIONS

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For the first time in the history of science and technology, a revolution has occurred, based on the recently developed ability to measure and manipulate matter on the nanometer scale in a skillful manner. At the nanoscale, Physics, Chemistry and Biology, Medical sciences, Materials science and Engineering converge to same principles. As a result progress in nanoscale will have far reaching impact and the next revolution in science and technology will depend on science interdependence. The future of nanotechnology is likely to continue in this interdisciplinary manner. This technology would directly benefit a common man when it comes to commercial use. But till then there is an immediate need to convert this science with proper technology. It has already established a beachhead in the economy.

In response, we have discovered and explored a new bio-safe and bio-compatible route for the synthesis of oxide nanomaterials using water as solvent as well as source of oxygen. The use of water as a reagent is particularly attractive because it is safe, inexpensive, environmentally benign and bestowed with many virtues especially under supercritical conditions. The simple and straightforward route is based on simple reaction of water and metal powder at relatively low temperature. Since water is regarded as a benign solvent and non toxic, the product (nanostructures) could be used safely for biomedical and other applications. The structural and surface morphology has been ascertained by the versatile equipments. In addition, the method is simple, straightforward, fast, economical, environmentally benign, involves green chemistry, which can make it suitable for scale large production. The prospects of the process are bright and promising. There are number of applications which shall be discussed during the talk.

# MECHANICALLY ACTIVATED COMPOSITES BASED ON TRANSITION METAL OXIDES: DEFECT STRUCTURE, REACTIVITY, APPLICATION POSSIBILITIES

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The mechanical activation (MA) of transitions metal oxides X=CuO, $Bi_2O_3$, $MnO_2$, $V_2O_5$, $MoO_3$, $CeO_2$or composites Al/X and CuO/$CeO_2$ leads to formation of non-equilibrium defects. In the self-review the structure and reactivity of these defects were investigated by different methods (XRD, SEM, TEM, ESR, sorption, DSC, TG, etc.). MA of individual oxides was accompanied by formation of nanosizes ($MoO_3$, $MnO_2$)or submicron sizes ($V_2O_5$, $Bi_2O_3$ and CuO) particles with crystalline size close to tens nm, microstrains, point defects, and “weak bonding” oxygen. The significant attention was paid to the investigation of “week bonding” oxygen properties. The influence of “weak bonding” oxygen on the reactivity of two types of MA nanocomposites: termites systems Al/X ($X_1$=$MoO_3$, CuO, $MnO_2$, $Bi_2O_3$) and catalytic active system CuO/$CeO_2$ will be discussed. For Al/CuO the optimal dose of MA with the highest value of experimental heat effect, burning velocity etc., was observed, where a sufficient defect density in the components and good mixture homogenization were ensured, but the degree of MA-induced conversion did not large. Advantages and disadvantages of mechanochemical methods for preparation of 3 types of composites (thermite systems Al/X, catalytic active systems CuO(Cu)/$CeO_2$ and materials for supercapacitors (X/C)) for applied purposes will be discussed.

# EFFECT OF PRECURSORS NiMnCoOx ON THE MECHANOCHEMICAL SYNTHESIS OF CATODE MATERIAL $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

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Various traditional methods may be used to fabricate NMC cathode materials, the most successful methods are the sol–gel, co-precipitation and solid-state methods. As a rule, the synthesis is carried out in two stages. The solid state method attracts producers of cathode materials by of its simple preparation procedure. A number of techniques have been proposed that blur the boundaries between solid-phase and solution technologies. For example, crystal hydrates of d-metals are used: lithium nitrate, nickel acetate, cobalt acetate, and manganese acetate with citric acid addition as solid complexing agent. The process cannot be attributed to solid-phase synthesis, because at the stage of mixing of crystalline hydrates of the initial salts, their mutual dissolution takes place in the crystallization water to form a gel. Then, when drying the resulting gel and its heat treatment occurs, a typical oxidation-reduction reaction of the nitrate-citrate-acetate complex takes place, which can be classified as the SCS.

In this paper, we investigated the effect of the initial reagents on the quality of the cathode material $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, obtained by traditional solid-phase synthesis. In experiment A, the mixed oxide $NiMnCoO_x$ was prepared from a solution of cobalt, manganese and nickel nitrates, synthesized in the SCS reaction with glycine and citric acid. The milling and mixing of NiMnCoOx precursors with lithium carbonate was carried out by a mechanical activator 2S. In experiment B, oxides of cobalt, manganese and nickel were mechanically activated with lithium carbonate. Experiment C performed a single-stage solid-phase synthesis of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ from the main carbonates of manganese, nickel, cobalt and $Li_2CO_3$. After grinding, the samples were annealed at 900-930°C. The crystal structure, morphology and specific surface area of the obtained samples of the cathode material are studied.

# NEW SODIUM-CONTAINING CATHODE MATERIALS: MECHANOCHEMICAL SYNTHESIS AND ELECTROCHEMICAL PROPERTIES

N.V. Kosova

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In recent years, investigations in the energy saving field have been focused on the development of the sodium-ion batteries since sodium is much more abundant, ecologically sound, and cheaper than lithium. The main issue for the Na-based systems is their lower energy density as compared to the Li-ion systems, and a smaller choice of the electrode materials available for sodium technology. There is a significant interest in polyanion cathode materials as safe alternatives to conventional oxide cathodes. In the present work, the $Na_3V_2(PO_4)_2F_3$ (S.G. $P4_2mnm$) [1], $Na_2FePO_4F$ (S.G. *Pbcn*) [2], $Na_2FeP_2O_7$ (S.G. *P*-1) [3], and $Na_4Fe_3(PO_4)_2P_2O_7$ (S.G. $Pn2_1a$) [4] cathode materials with different crystal structure were prepared by mechanochemically assisted solid-state synthesis. Their structure and electrochemical properties were investigated by a complex of physico-chemical methods. Electrochemical cycling was performed both in Na and Li cells. When cycling in Li cells or under treatment in solutions with Li salts, a partial $Na^+/Li^+$ ion exchange occurs. The as-prepared mixed $Na^+/Li^+$ materials can be used as matrices for lithium-ion batteries with increased operating voltage. The immobile $Na^+$ ions act as pillars, thus contributing to the structural stability of these cathode materials during cycling.

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# THE STRUCTURE AND ELECTROCHEMISTRY OF THE MIXED SODIUM-LITHIUM VANADIUM FLUOROPHOSPHATES $Na_{3-y}Li_yV_2(PO_4)_2F_3$

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$Na_3V_2(PO_4)_2F_3$ is a promising polyanion cathode material for sodium–ion batteries with a three-dimensional framework structure [1]. Thanks to the stable framework such materials are able for cation and anion substitution that permits using them as the matrices for the lithium intercalation. In the present work, we studied the $Na^+/Li^+$ substitution in $Na_3V_2(PO_4)_2F_3$ using different synthesis approaches (equilibrium and non-equilibrium) and the electrochemical properties of the as-prepared mixed compositions.

The mixed Na/Li compositions $Na_{3-y}Li_yV_2(PO_4)_2F_3$ were prepared by the solid-state reactions, the chemical and electrochemical Na/Li ion exchange. For the solid-state process, the reagent mixtures with various Na/Li ratios were preliminary mechanically activated using a high-energy AGO-2 planetary mill and then annealed in an Ar flow. Chemical exchange was performed in the organic solution of LiBr as a $Li^+$ source, while the electrochemical exchange was realized in the electrochemical cell with Li metal anode and $LiPF_6$-based electrolyte. Crystal structure, morphology and electrochemical properties of the materials were analysed by XRD, SEM, EIS, galvanostatic cycling and cyclic voltammetry.

It was shown that during electrochemical cycling in the Li cell $Na_3V_2(PO_4)_2F_3$ prefers the mixed Na/Li (de)intercalation with the predominant $Na^+$ one. The amount of the $Na^+$ ions, electrochemically replaced by $Li^+$, does not exceed 16 mol. %, which coincides with that obtained after chemical ion exchange. The solid-state reactions result in the formation of the mixed $Na_{3-y}Li_yV_2(PO_4)_2F_3$; the crystal structure of the pristine material is preserved. The lattice parameters of the mixed phases decrease vs. Li content, pointing to the occurrence of the partial substitution of Na by Li. These samples show a considerable increase in electric conductivity and high-rate capability in comparison with pure $Na_3V_2(PO_4)_2F_3$.

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# MA SHS TECHNOLOGY FOR SPHERICAL POWDERS OF A HEAT PROOF NiAl BASED ALLOY PRODUCTION FOR ADDITIVE TECHNOLOGIES

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This research has been aimed at development of an effective way of obtaining close-cut-fraction micropowders from new heat-resistant alloys based on nickel aluminide in order to make geometrically complicated vital parts of airspace machinery using additive production technologies.

The promising NiAl–Cr–Co-Hf CompoNiAl M5-3 alloy composition was chosen in order to obtain close-cut-fraction micropowders from materials of the new generation for additive technologies. Elemental synthesis with addition of the functional additive NaCl was used as a way of obtaining powders from heat-resistant alloy based on nickel aluminide (CompoNiAl-M5-3) composition.

The optimal mode of the MA was searched using planetary mills Pulverisette 5/2 (Fritsch, Germany), MPP-1 (Technics and Technology of Disintegration, Russia) and Activator-4M (Activator, Russia). The reaction mixture of a specified composition was activated at equal parameters: a balls-material ratio of 10:1 and a drum filling coefficient $\varphi$ =0.55. The comparative researches of the structure and distribution of the components in the MA mixtures and synthesized samples have shown that the treatment of the initial mixture in the Activator-4M for 12 minutes is the optimal mode. Experimental researches of grinding the synthesized CompoNiAl-M5-3 composition alloy samples obtained through the elemental synthesis and washing them from the salt have been conducted. The optimal mode of the disintegration that ensures the maximal output of the 20-45 μm fraction has been found. Powders of the said fraction have been tested when researching into the spheroidization process in an electroarc plasmatron reactor.

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# SYNTHESIS OF NANO- AND MICRON-SIZED METAL POWDERS FOR ADDITIVE TECHNOLOGIES

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The development of innovative additive manufacturing techniques and expanding their application areas have recently progressed rapidly. Additive equipment can now use metals, polymers, ceramics, composites or other powder materials to create a range of functional components. Both chemical and mechanochemical methods for production of nano/micro metal powders, precision alloys and ceramics which can be used in 2D and 3D printing have been developed at the ISSCM SB RAS together with their partners. Reduction of organic or inorganic salts of metals in a high-boiling organic liquid is among the methods of preparation of the nano- and micron-sized metal powders.

A modified polyol method for the synthesis of metal powders (silver, copper, nickel, bismuth, cobalt, etc.) and alloys with the particle sizes ranging from 10 nm to 10 microns has been developed. It consists in preparing metal carboxylates via the exchange reaction between sodium salt of an organic acid and aqueous solution of the corresponding metal nitrate followed by their reduction in a polyol medium to the metallic state. Thus, reduction of the silver neodecanoate extract in benzyl alcohol at 180°C was shown to result in the formation of trigonal and hexagonal silver plates of 0.5–2 μm in wideness and 40–60 nm in thickness and decahedral and other polyhedral silver particles of 200–500 nm in size. The optimal reaction conditions, when reducing the copper 2-[2-(2-methoxyethoxy)ethoxy]acetate extract in benzyl alcohol, resulting in the formation of copper nanoparticles of 8−15 nm and spheres ~1-5 μm in size have been found. Bismuth spherical nanoparticles of 100–300 nm in size were synthesized via the reduction of the bismuth caprylate extract in benzyl alcohol. The nanoparticles thus prepared are stabilized with carboxylates due to which they are well dispersible in polar solvents, in particular in alcohols, and have a high potential for use in inkjet printing. The method developed allows getting high yields of the product and control of the required characteristics, such as particle size and size distribution, with low production cost and ease of scalability. The powders can be used for the preparation of conductive inks for 2D printing, pastes, adhesives and polymers, as well as for fabrication of the 3D layer-by-layer structures.

# BORON NANOPARTICLES PRODUCTION BY ULTRASONIC CAVITATION

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One of the main challenges in boron neutron capturing therapy (BNCT) for cancer is the search for boron delivery agents that satisfy the main requirement – containing a large number of boron atoms to achieve a therapeutic concentration in the affected tissues (20-35 μg per 1 g of tumor tissue, which corresponds to ~ 10 billion boron atoms per cell).

Modern boron-containing molecules are compounds of polyhedral boron hydrides with a maximum number of atoms ~ 12 [1]. To increase BNCT efficacy, it is necessary to increase the number of atoms of the targeting agent in the compound solution. The use of boron nanoparticles as agents for BNCT could significantly improve the efficacy of the compound. With a nanoparticle diameter of 3 nm, the number of boron atoms will be ~ 120 thousand, and with a diameter of 50 nm - about 2 million.

We propose a new method for obtaining boron nanoparticles by cascade ultrasonic dispersing/destruction (USD) of elemental boron micron particles (10-20 microns) in an aqueous medium. The use of water as a dispersion medium is one of the main advantages, since the final form of the compound is presented as an aqueous particle dispersion, in contrast to traditional methods of nanoparticles synthesis, where they are obtained in the form of powder [2]. Under ultrasound, large boron crystallites (X-ray crystallography data) degrade and nanoscale particles less than 100 nm are formed (DLS and TEM data).

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# HYBRID NANOCOMPOSITES FOR EXTRA WEAR RESISTANT DIAMOND CUTTING TOOLS

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Diamond cutting tools play an important role in machining of various materials, such as natural stone, concretes, asphalt and steels. The tool is a composite material with diamond grains incorporated into the metal, ceramic, or polymer binder. Promising way to design enhanced metal binders is mechanical alloying of elemental powders with simultaneous nanoparticles reinforcement.

We offered the new way of advanced binder design, which involved hybrid reinforcement with different types of nanoparticles. The various nanoparticles (carbon nanotubes, boron nitride h-BN, nanoparticles of tungsten carbide WC) and their combinations were embedded into metallic matrices and their mechanical properties were determined in experiments. The strong positive effect of this combined nanoreinforcement was caused not by accumulation of mechanical effects, but rather by combination of different structure controlling effects, namely, grain size reducing effect due to carbon nanotubes introduction, mechanical reinforcement because of tungsten carbide, and lubricating properties of h-BN particles.

The wear resistance of diamond tools with metallic binders modified by various nanoadditives was estimated. 3D hierarchical computational finite element model of the tool binder with hybrid nanoscale reinforcements was developed and applied for the structure properties analysis of the binders.

It was shown that the metallic nanocomposites with hybrid nanoadditives ensured the highest mechanical properties and also the highest wear resistance of the machining tools with the nanocomposites used as binder.

# NANOCRYSTALLINE MECHANICALLY ALLOYED Fe-Co-Ni BINDER WITH HIGH STRENGTH AND WEAR RESISTANCE FOR DIAMOND TOOLS

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The diamond tools are widely used in the construction and mining industries. The working layer of these tools is typically made of a composite material: diamond grains surrounded by the metal matrix (the binder). The binder has several important functions: it holds the diamond in the working layer, is responsible for the redistribution of the bearing load, and ensures the conditions for working layer renewal (the wear rate of the binder being equal to that of diamond), which constantly maintains the high performance properties of the tools. Generally, binders with advanced mechanical properties (bending strength, hardness, toughness) make the tool performance higher through better diamond retention.

The aim of this study is designing of new binder composition based on Fe-Co-Ni alloy. The superior mechanical properties of this binder are provided by two approaches. First, Fe-Co-Ni powder mixture is prepared by means of mechanical alloying in high energy planetary ball mills. Thus, it provides formation of a nanocrystalline structure, solid solution strengthening of the α-Fe matrix and leads to accumulation of high concentration of lattice defects. Second, the Fe-Co-Ni basic composition is reinforced with nanoparticles of different kind: WC, hBN and carbon nanotubes. Using of all three types of nanoparticles simultaneously involves three different strengthening mechanisms – matrix grain refinement, dispersion hardening and solution strengthening.

Also, in this study an attempt to investigate, how nanoparticles affect the binder deformation mechanisms, through in-situ mechanical tests during TEM observation was done. The multi-element 3D computer models that set the relationship between the structure, nanomodifier distribution, morphology and the mechanical properties of a Fe-Co-Ni binder were built.

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# FORMATION AND PROPERTIES OF Mn-SUBSTITUTED CORDIERITES UNDER MECHANOCHEMICAL TREATMENT

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Mn-substituted cordierites, $Mn_xMg_{2-x}Al_4Si_5O_{18}$ (x = 0-2) were found to show good catalytic activity in high-temperature ammonia oxidation reaction, probably, due to the formation of $Mn_2O_3$ on the cordierite surface [1, 2]. The substitution degree, calcination temperature and preliminary mechanical treatment could affect the properties of Mn-cordierites and catalytic activity as well.

In this work we study the effect of mechanochemical activation of starting minerals (kaolin, gibbsite and $MnO_2$) on the crystallization behavior, sintering and properties of Mn-substituted cordierite $Mn_2Al_4Si_5O_{18}$. For this purpose, investigation of different grinding time (0-6 min) in a planetary mill APF-5 was considered in order to characterize different phases formed and final properties of the sintered material including the catalytic activity in ammonia oxidation reactions at 700-900$^o$C.

The thermal analysis shows that activation duration affect the dehydration of the initial reagents, as well as the formation of phases of mullite and cordierite shifts towards lower temperatures. On the other hand, an increase in $MnO_2$ reduction temperature occurs. It indicates a possible interaction of manganese and aluminum oxides during the long-term treatment and further Mn-Al-spinel phase formation (according to XRD data).

So, mechanochemical activation of starting minerals for 1.5-3 min results in formation of well-crystallized Mn-substituted cordierite after calcination at 1100-1150$^o$C with low specific surface area, high open porosity and surface enrichment with Mn cations that shows high activity in ammonia oxidation reaction.

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# CONSTRUCTION OF CERAMOMETAL POROUS CATALYSTS AND SUPPORTS FROM POWDERED ALLOYS PREPARED BY THE MECHANOCHEMICAL METHOD

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Design of porous cermet matrix MeAlO/MeAl-based composites (Me = Cr, Fe, Co, Cu) based upon their studies by XRD, SEM with mapping, adsorption, thermal conductivity, mechanical strength, permeation and catalytic activity measurements will be presented. Basic preparation stages of porous cermets from MeAl (Me = Cr, Cu, Co, Fe) powders are elaborated using mechanical alloying (MA) of Me-Al powders and soft hydrothermal treatment of mechanically alloyed blends followed by thermal treatment, which allows controlling their mechanical, thermophysical and textural properties. The metal particles randomly distributed in the oxide matrix improve functional properties of monoliths making them promising for different application in catalysis. Ceramometal monoliths with metallic particles (up to 80 wt.%) randomly distributed in the oxide matrix are characterized by the hierarchical pore structure with developed ultramacropores, which provides their high permeability. Mesoporosity of ceramometal monoliths was developed by incorporation of mesoporous components into their structure. Monolithic catalysts based on these cermet substrates were shown to be promising for different fields of application in catalysis. Catalytic properties are demonstrated in reactions of deep and partial oxidation, steam reforming of methane and CO, etc. Relations between parameters of MA and properties of ceramometals will be discussed.

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# MECHANICAL STRAINS EFFECTS IN SOLID ELECTROLYTES

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There are two main approach to control electrical properties of solid electrolytes (besides variation of external pressure and temperature): (a) homogeneous doping with impurities leading to the formation of solid solutions and (b) introduction of heterogeneous additives (heterogeneous doping) which generate a large number of interfaces. It should be emphasized that both homogeneous and heterogeneous doping results in strains of different origin. In solid solutions the doping may result in a strong shift of the phase transition temperatures. There is a similarity between a PT - diagram of pure substance and the phase diagram of solid solutions obtained by doping this compound with some additives. Really this effect may be explained by positive or negative strains (positive or negative “concentration pressure”) in the crystal lattice generated by introduction of large- or small-sized atoms or ions into the host matrix. The change in the Gibbs energy of the crystal internally deformed by inclusion of the dopant atoms (or ions) may be expressed as $dG \approx -SdT - \sigma_{ij}de_{ij} + \mu dN$, where $\square_{ij}$ and $e_{ij}$ are strain and deformation contributions which may be expressed as tensor components. Assuming that the contribution of strains to the overall Gibbs energy varies proportionally to the dopant concentration, one can introduce the concept of the mechanochemical potential $\tilde{\mu}_{\sigma k} = \mu_k^0 - \sigma_{ij}\Delta e_k$, where $\square_k^0$ is the standard value and the second term is the change in the elastic energy of the crystal due to introduction of the dopant atom of *k*-th type; $\square e$ is the deformation of the lattice caused by the dopant which depends on the volume misfit between the host and guest atoms (or ions). The introduction of the dopants may lead to both increase or decrease in the $\square$ value as a function of the strains sign and cause the change in the migration energy. For charged species the mechanochemical potential is related to the electrochemical potential $\tilde{\mu}_i = \mu_i^0 + q_i\varphi$ that allows one to estimate the effect of the ionic size on the surface potential values as well as grain boundary resistance in solid electrolytes.

# SYNTHESIS OF PROTONIC CONDUCTORS BY MECHANOCHEMICAL ACTIVATIONS

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Proton-conducting oxides including those with mobile oxygen are used in design of proton-conducting membrane reactors to produce pure hydrogen from syngas obtained by fuels reforming [1].For design of asymmetric supported proton-conducting membranes, the most promising materials are nanocomposites comprised of oxides with fluorite structure such as lanthanide tungstates combined with metals or their alloys.

In this work we consider complex oxides such as $Nd_{5.5}WO_{11.25-\delta}$, $(Nd_{5/6}La_{1/6})_{5.5}WO_{11.25-\delta}$, $Nd_{5.5}W_{0.5}Mo_{0.5}O_{11.25-\delta}$ and their nanocomposites with copper-nickel oxides/alloys. Complex tungstates have been prepared using mechanochemical activation of starting oxides in a high-power planetary ball millAGO-2 (1200 rpm). To prepare the powder of NiCu alloy, the mixture of NiO and CuO obtained by decomposition of the mixed nitrates was reduced in the flow of $H_2$ at 350°C. Studies of tungstates and nanocomposites genesis and structural properties using XRD, SEM, IR and Raman spectroscopy have demonstrated that mechanochemical activation results in formation of well crystalized tungstates fine powder already after 20 minutes activation without sintering. Further high-temperature calcination at 1300°C also leads to the formation of single-phase samples with fluorite structure. Transport properties were investigated by oxygen/hydrogen isotope hetero exchange, high oxygen and proton mobilities were shown. Conductivity was investigated by 4-electrode technique. After high-temperature sintering of nanocomposites based on proton conductors and NiCu alloy, proton conductivity values ~ $10^{-4}$ S/cm at 400 °C were achieved.

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# NEW TYPE OF COMPOSITE PROTON ELECTROLYTES SYNTHESIZED BY MECHANICAL ACTIVATION

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Cesium dihydrogen phosphate is one of the most conductive proton electrolytes at intermediate temperatures and is of great scientific and practice interest as a proton membrane for fuel cells. It has the highest value of proton conductivity, $6\cdot10^{-2}$ S•cm$^{-1}$ in the superionic phase. The conductivity of the low temperature (LT) phase ($P2_1/m$) is less than $10^{-6}$ S•cm$^{-1}$. Heterogeneous doping with highly dispersed oxides ($SiO_2$, $SiO_2$-$P_2O_5$) allows to increase the conductivity and obtain composites with improved mechanical and thermal stability due to oxide matrix. To suppress the dehydration of $CsH_2PO_4$ in superionic phase the 30 mole% water partial pressure is necessary.

The main objective of the work is new approach for stabilization of $CsH_2PO_4$ superionic (Pm-3m) phase in composites at the lower water partial pressure. This work was directed to the investigation of microstructure, phase composition, electrotransport and thermal properties of new composite (1-x)$CsH_2PO_4$-xA electrolytes, where A=$SrZrO_3$ and $SnP_2O_7$ (x=0.1-0.8) at various water vapor partial pressures. The nanocomposites were synthesized by prolong mechanical mixing of the stoichiometric quantities of $CsH_2PO_4$ and dispersed matrix followed by heating at ~210$^{o}$C.

According to X-ray diffraction, the crystal structure of $CsH_2PO_4$ was preserved in the nanocomposites, but its' structural and thermodynamic properties differ markedly due to the disordering and partial amorphization with the increase of additive content. So the significant increase of conductivity up to 1-3 orders in the LT phase was observed. The conductivity in superionic phase doesn't depend on the content of heterogeneous additive up to x=0.2 and decreases with x increase. The composites have high conductivity ~$10^{-2}$ S/cm and thermal stability during a long term storage at 230-260$^{o}$C at the lower water partial pressure (10-15 mol %) in comparison with individual $CsH_2PO_4$. The comparison of two types of proton composites has been carried out. The introduction of highly dispersed $SrZrO_3$ and $SnP_2O_7$ with high sorption of water vapor and retention at elevated temperatures was shown to change the thermodynamic characteristics for dehydration of $CsH_2PO_4$ (Pm-3m). Such effects are very important for creating intermediate-temperature proton membrane for the fuel cells.

# PROTON-CONDUCTIVE POLYMER MEMBRANES BASED ON $CsH_2PO_4$

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One of the most important direction of improvement of electrochemical characteristics of Solid Acids Fuel Cells is the using the thin-film flexible proton membranes [1]. Similarly to composites based on acid salts and highly dispersed inorganic oxide the conductivity of $CsH_2PO_4$- polymer systems is determined by the morphology of the particles and the energy of adhesion [2]. The mechanochemical treatment improves the synthesis conditions of proton hybrid membranes with the uniform distribution of dispersed particles.

The aim of this work is investigation of the electrotransport, structural, thermal properties and the mechanism of proton conductivity of the polymer membranes of a new class based on $CsH_2PO_4$ and F- containing thermal stable polymers. As polymer matrix polytetrafluoroethylene (PTFE) and copolymer of vinylidene fluoride with hexafluoropropylene (SKF) were firstly used. The conductivity measurements were carried out in conditions with the different humidity for the suppression of $CsH_2PO_4$ dehydration.

The small content of the polymer matrix was shown to result in the conductivity close to $CsH_2PO_4$ superionic phase. However the high polymer content (> 15 wt%) leads to the percolation threshold of the "conductor-insulator" type with the decrease of the proton conductivity. The phase compositions of the polymer electrolyte, unit cell parameters and particle size distribution have been characterized by XRD and electron microscopy methods. The addition of an organic polymer matrix was shown to result in a decreasing $CsH_2PO_4$ unit cell parameters, its’ particle size and the partial amorphization. The addition of optimal amount of polymer matrix provides the flexibility and thickness of the membrane, increasing of hydrolytic stability, gas permeability while maintaining high conductivity, which is perspective for fuel cells membranes.

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# COMPUTER DESIGN AND TESTING OF A SILICENE ANODE FOR A LITHIUM-ION BATTERY

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Silicene is a two-dimensional structure composed of a buckled hexagonal honeycomb silicon lattice. The ability of silicon to hold a large amount of lithium puts silicene in a series of the most promising materials for the anode of lithium-ion batteries (LIBs). An increase in the rate of the movement of lithium ions through silicene can be achieved through the use of silicene with vacancy-type defects. The effect of vacancy-type defects on the fillability with lithium of the channel formed by silicene sheets on the Ag (111) and Cu (111) substrates, as well as on the structural and kinetic properties of lithium, has been studied by the molecular dynamic method. The limit number of intercalated lithium atoms and their self-diffusion coefficient increase with the transition from the perfect silicene channel to the channel containing mono-, bi-, and tri-vacancies. The lithium structure in the channel was studied using the method of statistical geometry. The packing of lithium atoms in the channel turns out to be partially ordered due to the regular placement of some atoms that occupy places closer to the centers of hexagonal Si-cells. The $\sigma_{zz}$ stress in the sheets of silicene decreases during intercalation of lithium and increases at the final stage of deintercalation.

The performed studies showed that in contrast to crystalline silicon two-layer silicene does not experience an irreversible destructive effect caused by intercalation lithium. The computer experiment performed by us shows that for this purpose it is preferable to use silicene containing mono and bivacancies. It is the presence of these defects in the sheets of silicene that contributes to a significate increase in the capacitance of the electrode. Our results show that it is difficult to obtain capacitance values close to the theoretical value for the silicene electrode. It is necessary to pay close attention to the substrate material, which will be used together with silicene, because the absorption properties of silicene, including binding energy with lithium, and the stability of silicene to cycling depend on the substrate material. In particular, copper can be considered as a relatively good material for use as such substrate, which allows obtaining a good silicene electrode capacity.

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# CREATION OF THIN OXYGEN MEMBRANES FOR PURE DISTRIBUTED MULTIGENERATION

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The mechanochemical ceramic method (MCM) for the design of nanomaterials has its own specific features. The most significant features of mechanochemical nanopowders are a wide distribution of particles in size (100 nm - 100 μm), complex structure (aggregates <2 μm with relative density *RD* ~ 0.8, secondary agglomerates with *RD* ~ 0.7), huge free volume ~ 10% in crystal lattice (vacancy defects), a large content of charged (for example, $M^{2+}$ cations in the $M^{3+}$ matrix) and neutral point defects ($ZrO^{2+}$ in $ZrO_2$). Specific features of powders are related to the mechanism of mechanosynthesis, which occurs at the contact of particles under mechanical loading above a certain threshold through an intermediate so-called dynamic state *D**. *D** can be represented in the form of growing rollers from atoms of interacting phases with nondiffusion mass transfer accompanied by intense electron emission. Relaxation *D** under quenching during decompression leads to the observed products. Nanoscale crystallites with sizes up to 5-10 nm arise not as a result of grinding, but as a result of *D** relaxation as a structural component of aggregates and secondary agglomerates. For functional materials, the features of mechanochemical powders, as a rule, do not allow achieving record parameters for the whole set of properties. However, understanding mechanochemical processes makes it possible to use the unique capabilities of MCM in the design of dense functional materials, eliminating or significantly reducing the negative features of nanopowders. As a result of many years of research on the application of MCM to the creation of various functional materials, a nanocermet $\delta$-$Bi_2O_3$/Ag was chosen based on the best oxygen-ion and electronic conductors. This material is the most promising for the creation of IT oxygen membranes. The report will present the mechanism of nanocermet degradation due to the chemical interaction of stabilized bismuth oxide with a fluorite structure and silver, activated by the features of mechanochemical powders and catalysts such as Pd, Pt. A combination of new nanomaterials with highest parameters for creating thin ~10 μm membranes and a roadmap for design flexible membranes with an optimal architecture supported on a metal grid are proposed. Membrane stacks with a working temperature of about 550 C are able to provide the necessary oxygen flow for use in waste-free clean coal energy.

# DESIGN OF NEW NANOSTRUCTURED THERMOSTABLE $TiO_2$ OF ANATASE STRUCTURE DOPED WITH ALUMINA

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Titanium dioxide (anatase) is widely used as an adsorbent and support for the metal and oxide catalysts. It is also employed in materials converting solar energy into electricity and in chemical sensors. However, anatase is metastable and when the temperature is raised to 700 $^0$C it irreversibly converts to rutile form. It leads to a significant reduction of the surface area and changes the pore structure. In this regard, the increase of the thermal stability of $TiO_2$ (anatase) is an actual task.

The aim of this work is to study the effect of alumina on the formation of nanostructure of anatase during the heat treatment in a wide range of temperatures.

Titanium dioxide doped with $Al_2O_3$ (1-10 wt. %) were synthesized by incipient-wetness impregnation of anatase with an aluminium nitrate solution, dried in air, and then heated in air at 300-1000 $^0$C for 4 h. The physicochemical properties of the obtained samples were studied by XRD, HREM, and low-temperature (77 K) nitrogen sorption methods.

X-ray diffraction data show a significant increase in the anatase to rutile phase transition temperature in titania doped with aluminia. The calcination of $TiO_2$ doped with $Al_2O_3$ does not yield rutile until 950 $^0$C, while the rutile phase in undoped titania is detectable at 750 $^0$C. The unit cell parameters of anatase (“a” and “c”) in $TiO_2$ doped with alumina are not changes. According to HRTEM data introduction of additives of alumina into titania after the heat treatment at 500 $^0$C leads to the formation of nanocrystalline structure while undoped titania has a well-ordered crystal structure. The nanocristalline structure consists of intergrown fine anatase crystallites 5-7 nm in size separated by interblock boundaries, in which the aluminum ions are stabilized. This stabilization is due to the fact that in the area of boundaries anatase structure strongly disordered. Formation of $TiO_2$ with nanocrystalline structure stabilize the anatase phase at much higher temperatures (900-950 $^0$C) compared with the pure $TiO_2$. Increasing the thermal stability of the anatase phase leads to the keeping of a higher specific surface area and a developed porous structure at the high temperature.

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# THE INFLUENCE OF SILICON CARBIDE OBTAINED BY THERMAL DECOMPOSITION OF MONOSILANE ON THE PROPERTIES OF CAST POLYURETHANE

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The comparison of service properties of cast polyurethane (PU) before and after its modification by nanodisperse ceramic silicon carbide (SiC) particles has been carried out. SKF PFL-100 was used as a prepolymer. SIC nanoparticles ($d_{av.}$=50 nm) were produced by thermal decomposition of monosilane by the method of adiabatic compression of gas mixture (monosilane in argon (1:9)), into which acetylene was introduced in the amount of 2.5-15 vol. %. SiC nanoparticles coated with carbon shell and without it were produced.

The introduction of nanodisperse SiC into PU without carbon shell in the amount of less than 1% leads to the increase of tensile strength and relative elongation (Table).

Table. Characteristics of polymer composites based on PU and SIC nanoparticles

| Modifier | Modifier amount, % | Tensile strength, MPa | Relative elongation, % | Size of polymer grain, µm |
|---|---|---|---|---|
| SiC, without carbon shell | 0 | 28,1±1,2 | 625,1±16,3 | 5,2±0,7 |
| | 0,0015 | 37,4±0,4 | 695,6±13,2 | 2,4±0,4 |
| | 0,003 | 36,7±1,3 | 802,1±24,1 | 2,7±0,4 |
| | 0,005 | 36,2±0,5 | 787,3±10,0 | 4,1±0,9 |
| | 0,01 | 30,8±0,7 | 669,6±10,0 | 4,8±0,8 |
| | 0,03 | 30,5±0,5 | 792,2±15,9 | 4,9±0,9 |
| | 0,05 | 30,2±1,0 | 663,0±16,3 | - |
| SiC, coated with carbon shell | 0,001 | 25,2±0,1 | 741,5±25,3 | 3,4±0,9 |
| | 0,005 | 25,4±0,7 | 746,4±72,4 | 4,8±0,4 |
| | 0,01 | 27,5±0,2 | 811,6±8,4 | 4,5±0,9 |
| | 0,05 | 24,9±0,8 | 649,9±47,1 | 3,5±0,8 |
| | 0,1 | 24,3±0,1 | 775,0±35,2 | 3,5±0,9 |

Modification of PU samples with nanodisperse SiC coated with a carbon shell did not lead to a significant change in the tensile strength (Table).

Strengthening of polymer materials takes place as a result of the reduction in the grain size of the polymer when introducing the modifier particles. These particles to change the properties of the material should be wetted with this material. Otherwise, they act as structural defects. SiC particles coated with a carbon shell probably have a worse wettability in contrast to the same particles without a carbon "coat". Thus, SiC particles coated with a carbon shell practically do not affect the grain size of the polymer, which is confirmed by the data in Table: the change in the strength of these samples lies within the confidence interval.

# COMPARISON STUDIES OF LABORATORY AND INDUSTRIAL MILLS AND SCALE APPLICATION OF LABORATORY ACHIEVMENTS

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One of the reasons of slow advancement of mechanochemical technologies involves transferring of the laboratory results to an industry. The most part of scientific research are curried out with laboratory activators and mills having productivity several dozens of grams per minute while activators with a productivity of 5 - 500 kg per hour are necessary for medium-tonnage production. The input of mechanical energy in such devices is much less, than in laboratory mills. For this reason, a considerable part of mechanochemical reactions which proceed in laboratory devices at the moment won't be able to be reproduced in industrial scale. For successful scaling of laboratory mechanochemical processes it is necessary to answer two questions. The first is what parameters one should be used to carry out mechanochemical processes and mechanical activation in laboratories if we want to commercialize our researches in the immediate future. The second question is what modes of processing of substances and materials should be used in laboratory for successful modeling of industrial processes. For the solution of these tasks we have used river sand as a tested matter, which can be found in the many countries. As physical and chemical characteristics for comparison mechanical treatment by laboratory and industrial mills we have proposed the specific surface, coherent scattering region (CSR), the average size of particles. Solubility of sand in alkali solution is chosen as a character chemical property depending on the specific surface size of particles and imperfection of matter.

# APPLICATION OF MAN-MADE WASTES AS FILLERS FOR POLYMER MATERIALS

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In recent years the technologies of new composite materials based on filled polymers become widespread. The simplicity of the process has determined a new direction of production - the synthesis of materials which imitate natural stone. The material's strength, aesthetics, non-flammability, lack of design constraints determined the wide use of artificial stone in the manufacturing of construction and sanitary-technical products. The technical properties of such composites depend not only on the polymer matrix but also on the properties of the fillers. By combining different types of fillers manufacturers manage to get varieties of artificial stone with unique physical and chemical properties.

The purpose of this investigation was to compare the behavior of mechanically activated fillers based on fly ash and eggshell in the polymer matrix of polyethylene terephthalate (PET) compared to non-activated analogs, as well as natural materials. It was shown that for both types of fillers the mechanical activation promotes an increase in the samples strength. The physical and chemical properties of the fly ash material after intensive grinding in planetary mills are considered by methods of optical and electron microscopy. It is established that the mechanically activated filler, unlike its non-activated analog, structures the polymer matrix, providing an increase in the performance characteristics of the composite material, which in the authors’ opinion is due to the more interaction of the carbon of the ash material with the active groups of the polymer.

# RECOVERING OF SOLID WASTE BEARING LEAD OR ZINC BY MECHANOCHEMICAL EXTRACTION IN ALKALINE SOLUTION

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Considering that only Zn and Pb can be dissolved effectively in caustic alkaline solution, it should be of great significance to use the alkaline processes to leach Zn and Pb selectively from solid waste and secondary resources bearing lead or zinc. But the sphalerite and zinc ferrite in solid waste such as ore tailing or electric arc furnace (EAF), and lead atoms contained in lead glass, are very stable and insoluble in alkaline solution under ordinary temperature and pressure conditions.

This study evaluates the efficiency of using mechanical activation for the extraction of Zn and Pb from solid waste bearing lead or zinc. The mechanochemical leaching is more effective in comparison with the chemical leaching of non-activated samples. It was found that over 82% of Zn can be extracted from lean zinc ores containing sphalerite with lead compound as additive; more than 70% Zn can be extracted by mechanochemically reduced in EAF dusts. Around 67% of Pb was released after mechanically activation without iron, while more than 90% of Pb in the glass can be extracted after mechanochemical reduction with iron. High purity lead or zinc powder can be obtained by electrowinning from the leaching solution. The Pb and Zn-depleted solution can be recycled into the leaching step. These results may be used to further develop a hydrometallurgical process for recovering zinc or lead from solid waste bearing lead or zinc in alkaline solution.

# REGULARITIES IN THE GROWTH OF BIOCOATINGS WHEN DEPOSITED BY THE MICROARC OXIDATION OF MECHANOCHEMICALLY SYNTHESIZED STRONTIUM-SILICON-SUBSTITUTED HYDROXYAPATITE

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The work was aimed to investigate the regularities of the formation of the calcium phosphate (CaP) coating structure, composition and properties when deposited of the strontium-silicon-substituted hydroxyapatite (Sr-Si-HA) by the microarc oxidation (MAO) method. The coatings were formed on the pure titanium substrates by the MAO method in the anodic potentiostatic mode under the following parameters: the pulse time of 100 μs, the frequency of 50 Hz, the MAO time up to 10 min, and the pulsed voltage vary from 150 to 400 V. The electrolyte contained the phosphoric acid, the calcium carbonate, and Sr-Si-HA nanopowder ($Ca_{9.5}Sr_{0.5}(PO_4)_{5.5}(SiO_4)_{0.5}(OH)_2$) synthesized by the mechanochemical method.

By the scanning electron microscopy (SEM) it was shown that all coatings have a complex structure containing the multiple branched pores and the heterogenic surface morphology represented by the spherical structural elements (spheres) of 10-50 μm in size and plate-like crystals (up to 15 μm). The increase in the pulsed voltage is attended with the increase in the intensity of microarc discharges, resulting in a linear increase in thickness, roughness, surface porosity and the size of the structural elements. X-ray diffraction (XRD) showed that the coatings deposited at 150-250 V have an X-ray amorphous structure. When the voltage increase from 300 to 400 V the amorphous-crystalline structure is formed and amount of crystalline phase of monetite $CaHPO_4$ in the coatings increases. Energy-dispersive X-ray spectroscopic (EDX) revealed that with increasing MAO voltage the Sr and Si contents through the coating surface don’t change and equal to ~ 0.76 and 0.55 at.%, respectively. In this case, the Sr and Si contents in the areas of the plate-like crystal accumulation increase from 0.76 to 0.98 at.% and from 0.55 to 1.23 at.%, correspondingly.

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# MECHANOCHEMICAL ACTIVATION OF HUMIC SYSTEMS

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Humic acids (HAs) of solid caustobioliths and soils exhibit sorption and detoxification properties against organic toxicants and heavy metals. The use of mechanochemical activation (MA) for the purpose of obtaining efficient sorbents is a promising method of modification of structure and properties of HAs. MA of peat was carried out in a planetary mill in the presence of a nanodisperse powder of iron oxyhydroxides: an amorphous $FeOOH \cdot nH_2O$ (23 ± 6.2 nm) and a crystalline $FeOOH \cdot Fe_2O_3$ (28 ± 9.5 nm) forms. Oxides, poorly ordered hydroxides and oxyhydroxides of iron and aluminum are constituent parts of soils responsible for the retention of ions.

The physico-chemical regularities of the sorption of petroleum products from the water surface by means of milled and mechanically activated peat samples were studied. An increase in the oil capacity by 2 - 2.5 times and a decrease in water absorption by 7 times have been established. The *S*-shaped type II sorption isotherms suggest the presence of a significant amount of meso- and macropores along with micropores in the samples, which allows one to make the supposition of the formation of an inhomogeneous surface with sorption centers of different chemical and physical nature which differ also in activity.

The effect of mechanical activation of peat on structural parameters of isolated Has in the presence of iron oxyhydroxides was investigated. Using the method of titrimetric titration significant changes were revealed in the content of hydroxyl and carboxyl groups in aromatic fragments of HAs in MA with $FeOOH \cdot Fe_2O_3$. An increase by 2 times in the number of hydroxyl groups is due to oxidation-reduction processes in the presence of air oxygen and $Fe^{3+}$. A significant decrease in the content of carboxyl groups is explained by complexation reactions. Based on the results of $^{13}C$ NMR spectroscopy in the fragmented composition of mechanically activated HAs, the fraction of aromatic fragments increases, which enhances their sorption ability to petroleum hydrocarbons.

# KINETIC PARAMETERS OF DEHYDRATION DURING MECHANOSYNTHESIS IN THE SYSTEM «ACID SALT – ZEOLITE»

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Joint mechanochemical activation of clinoptilolite with acid salts allows to obtain composites. The dehydration of the samples, reflected on the thermograms by the endoeffect in the region from 50 to 150 $^{o}$C, can serve as a parameter for assessing the degree of defectiveness of their structure [1].

The aim of the work was to determine the apparent activation energy $E_{akt}$, the pre-exponential factor A in the Arrhenius equation, and the reaction order n of the «acid salt - zeolite» composites. To achieve this goal, the following tasks were solved: 1) synthesis of the mechanocomposites based on clinoptilolite rocks of the Kholinsk and Shivirtuy deposits (Transbaikal region) and salts: $Na_2HPO_4$; $K_2HPO_4$; $(NH_4)_2HPO_4$; $KHSO_4$ (16 samples, weight ratio 1: 1, vibration attritor AVC-3, duration of mechanoactivation 3 and 7 minutes,); 2) registration of thermogravimetric (TG) and differential thermogravimetric (DTG) decomposition curves (m = 19-22 mg, t = 25 ÷ 850 $^{o}$C, platinum crucibles, dynamic argon atmosphere, heating rate 10 $^{o}$C/min, synchronous thermoanalyzer STA 449F1 NETZSCH; 3) calculating the reaction order by the Kissinger method and the apparent activation energy by the double logarithmic method (Broido); 4) the construction of kinetic curves and their approximation (correlation coefficient $R^2 \geq 0,922$) with the help of the most typical formal-kinetic equations from the data of TG and DTG.

Analysis of the results of linearization allows us to conclude that the methods of Broido and Yander are the most suitable for determining the basic kinetic parameters of dehydration of the investigated mechanocomposites. It is established that the dehydration of mechanocomposites proceeds, as a rule, according to the first order. For clinoptilolitic samples containing $KHSO_4$ and $K_2HPO_4$, dehydration is a diffusion-controlled process.

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# MECHANOCHEMICAL AND RADIATION TECHNOLOGIES FOR OBTAINING NEW REFRACTORY MATERIALS

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Products made of refractory materials are used in various branches of technology: aerospace, nuclear power engineering and many others. Goods are made of carbides, borides and silicides by means of powder metallurgy. However, powders of the indicated materials are poorly compressible due to their high hardness, so the products obtained through sintering have high porosity. A more promising method is the synthesis from initial materials, with simultaneous formation by means of additive technologies. The sources of energy are focused beams of electrons and laser radiation. The use of highly intense focused electron beams and infrared laser radiation allows one to heat a local volume of the substance within a fraction of a second. Mechanochemical treatment of hafnium and carbon powders leads at first to the formation of mechanocomposite with highly developed inter-phase surface, and then to the formation of carbide. Irradiation with the laser was carried out helically from the edge of the crucible to its center. Band width was 1 mm. One can see in the Fig. 1 that the use of mechanocomposites is more profitable for product manufacture according to additive technologies.

Fig. 1. The image of the surface formed as a result of laser irradiation of hafnium carbide (the left) and of Hf-C mechanocomposite (the right).

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# STRUCTURE AND PROPERTIES OF NICKEL-BASED SELF-FLUXING COATINGS, REINFORCED BY HARD REFRACTORY PARTICLES WITH HIGH NB CONTENT

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Self-fluxing alloys are widely used as materials for retailoring of worn-out parts details working in corrosive atmospheres or in abrasive wear conditions combined with high temperatures. Among huge variety of coating formation methods the electron and laser beam cladding techniques provide maximal efficiency. Furthermore, rapid solidification associated with these techniques is able to generate structures comprised of both stable and metastable phases. Additionally, high power of these sources permits to work with refractory metals like *Hf, Nb, Zr, Ta*. High-energy electron beam accelerator ELV-6, developed by Budker Institute of Nuclear Physics SB RAS (Novosibirsk) equipped with a system of injecting electron beam in the air atmosphere was used in current work. *Nb* combined with *B* was used as reinforcing adding to Ni-based self-fluxing alloy (77 % *Ni*, 15 % *Cr*, 3 % *Si*, 3 % *Fe*, 2 % *B*) in different relations (0, 5, 15, 35 % *Nb* combined with *B*). Coatings, obtained by cladding with electron beam, injected into the air have gradient structure (Fig 1a). It is shown that different structures were formed during cladding. Using XRD investigations, it was discovered the presence of such phases like γ-Ni (dendrites, Fig. 1), $Nb_6C_5$, $NbB_2$ (white and dark phases indicated on Fig. 1b). Futhermore, Nb addition leads to hardness and abrasive wear-resistance increasing.

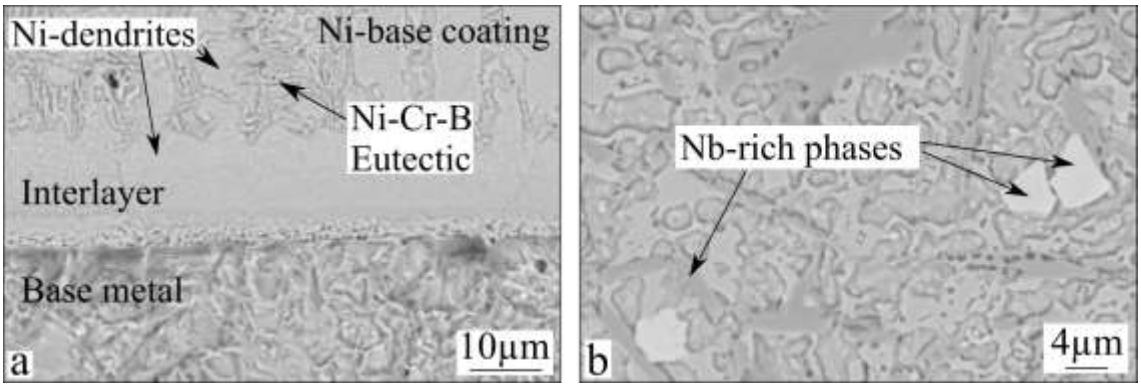

Fig. 1. Structure of self-fluxing nickel-based coatings, obtained by non-vacuum electron beam cladding of: a – 100 % Ni-based self-fluxing powder, b – “85 % Ni-based self-fluxing powder + Nb +B” mixture.

# INFLUENCE OF $Al_2O_3$-SLURRIES DISPERSION MODES ON CERAMIC SINTERING BEHAVIOUR

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It is well recognized that dispersion in an aqueous medium is one of the most effective ways to produce high-strength structural $Al_2O_3$-ceramic materials. On the other hand, realization of the process of mechanical activation (MA) is difficult. At the same time MA facilitate the intensification of sintering processes that leads to increasing characteristics of sintering material. In this paper influence of$Al_2O_3$-slurries milling time in a bead mill on sintered ceramics was investigated.

Submicron α-$Al_2O_3$CT 3000 SG powder produced by Almatis (d50 = 0.3 – 0.6μm, d90 = 2 – 3 μm) was used as a raw material. Dolapix CE 64 was used as deflocculation agent. Milling of 40% water slurries were carried out by bead mill MiniFer, Netzsch. A study of the sintering kinetics of experimental cylindrical samples was carried out with a horizontal dilatometer DIL 402 E / 7 (NETZSCH). The sample was heated up to 1650 °C.

The milling time of the alumina slurries was 1 hour (batch 1) and 3 hours (batch 2). The analysis of particle size distribution achieved by using a laser particle size analyzer "Microsizer" 201 As howed that the values for both batches of samples are similar and correspond to d50 ≈ 0.5 μm, d90 ≈ 1 μm. Therefore, dispersion limit is reached after 1 hour of the process duration. Beyond that point agglomerates and particles destruction process of powder was not proceeded. During the dilatometric studies it was found that the shrinkage growth rate increases from $3,88*10^{-3}$ 1/min to $4,22*10^{-3}$ 1/min with increasing milling time. It proves that a more active penetration of diffusion processes due to the increased density of crystal lattice defects. An increase in shrinkage from 17,7% to 17,9% is a consequence of the high activity of the material during sintering. It was found that the density of the sintered samples is 3,87 $g/cm^3$ (97,0% of theoretical values) and 3,89 $g/cm^3$ (97,4% of theoretical values) for the 1 and 2 batches, respectively.

The obtained data indicates about intensification of the sintering processes. Increase dispersion time of $Al_2O_3$-slurries in a bead mill led to an increase in sintering behaviour.

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# RELATIONSHIP BETWEEN MICRO-STRUCTURES AND WATER SOLUBILITY OF THE MECHANICALLY ACTIVATED PHOSPHATE ORE

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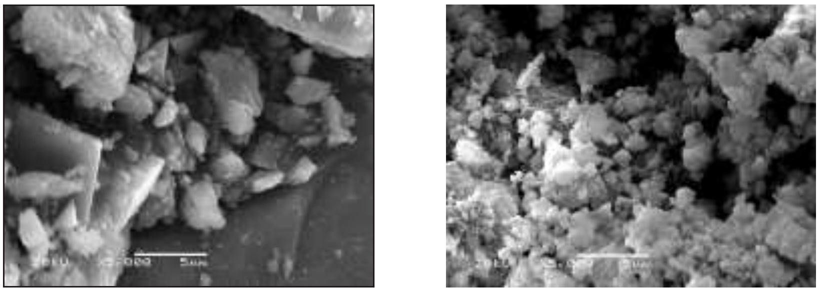
A mechanical activation of phosphate ore has been investigated with the planetary activator of AGO-2. The structures, particle size, chemical compositions and phase transition have been studied by means of size analyzer, infrared spectroscopy and X-ray diffraction methods. The images with and without activations showed in Fig. 1. The FT-IR spectra demonstrate significant decrease in the lattice constant of the activated samples due to the site substitution of $OH^-$ ions for the $F^-$ ions as shown in Fig. 2. XRD results showed that the samples after mechanical activation have gradually changed from crystalline to amorphous state as the grinding time increased, resulting in the storage of a large amount of distortion and surface energies, which in turn promoted the water solubility of the phosphorus samples which has been increased as high as 61.6%.



**(a) Before activation** **(b) After activation**

Fig. 1. SEM images of the samples.

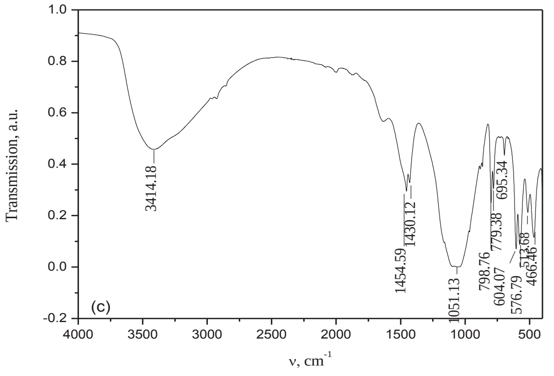


Fig. 2. FT-IR spectra of the samples.

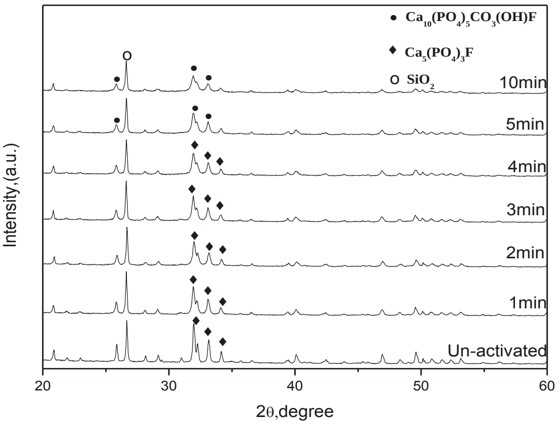


Fig. 3. XRD patterns of the samples.

# USE OF MECHANICAL ACTIVATION TO PRODUCE BISMUTH SOLUTIONS

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A keen interest in the fabrication of bismuth materials is due to their unique and desirable properties applicable to various fields. Typically, bismuth compounds are produced from metallic bismuth by dissolving it in nitric acid with a concentration of 7-9 mol/L, followed by hydrolytic purification at the precipitation stage as the basic nitrate. Bismuth oxide can also be used to prepare bismuth solutions. In this work, we systematically investigated morphology, chemical composition and physical parameters of bismuth oxides prepared under mechanical activation conditions. A preliminary study showed that the grinding of particles of metallic bismuth both in a mortar and in a grinding mill AGO-2 leads to a decrease in the average particle size to 30 μm. To prepare smaller particles, additional reagents, such as $Bi_2O_3$, $Na_2CO_3$, $NH_4HCO_3$, NaCl, $NaNO_3$, $NH_4NO_3$ and $C_{17}H_{35}COOH$, were used at the stage of grinding, followed by mechanical activation, washing with water and calcination in air. Mechanical activation of the mixtures make it possible to disperse the metallic bismuth, thereby lowering the bismuth oxidation temperature from (650±50) ºC to 200 ºC and completing its oxidation at a temperature of (350±50) ºC. It was found that when calcining a mechanochemically pretreated mixture of metallic bismuth and its oxide (20%) at 300 ºC, the total conversion of bismuth to oxide occurs in 12 hours, while at a calcination temperature of 400 ºC, it takes 1 hour. At mechanochemical activation of a mixture of metallic bismuth and sodium carbonate, followed by its washing with water, the resulted product consist mainly of bismuth oxide and oxohydroxycarbonate which can be used in producing mineral acids solutions of bismuth salts. At mechanochemical activation of a mixture of metallic bismuth and sodium chloride, followed by its washing with water, the resulting product consist of bismuth oxide and oxochloride, which can be used to produce bismuth chloride solutions. Preliminary mechanochemical activation of metallic bismuth with sodium and ammonium nitrate, or with stearic acid, can also be used to produce bismuth oxide. The specific surface area of bismuth oxide resulted from mechanochemical activation of metallic bismuth with various compounds was shown to vary within the range of 0.29-5.87 $m^2/g$.

# MECHANOCHEMICAL SYNTHESIS OF FINE CARBON COMPOSITE CONTAINING Mo2C/C: NEW APPROACH FOR THE HYDRODESULFURIZATION CATALYSTS PREPARATION

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Recently in the world there is an increased consumption of oil refining and petrochemistry products. As lower quality feedstock becomes more abundant, the additional challenges, such as catalyst deactivation and poisoning, arise. Therefore, one way to face these challenges is to develop catalysts that can better withstand the severe operation conditions prevailing in the hydrotreating of heavier gas oils. Transition metal carbides are considered as the new promising catalysts and have been widely investigated in recent years because of their unique electronic structure and high performance. Molybdenum carbides have similar catalytic properties to noble metal catalysts in various chemical reactions such as hydrogenation, hydrodesulfurization, and hydrodenitrogenation in petroleum refining.

In this work, molybdenum carbides were prepared using mechanosynthesis. The structure and catalyst activity of the molybdenum carbides were studied. Zirconium nitrate $ZrO_2(NO_3)_2 \cdot 2H_2O$, carbon black P145 and ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were used as starting compounds. Mechanochemical activation (MA) of reaction mixtures was performed in a water-cooled high-energy planetary mill AGO-2 (Novits Ltd., Novosibirsk, Russia). MA of the mixture of components was carried out at a 1000 $m/s^2$ acceleration of milling bodies for 15-30 min, the ball-to-powder mass ratio - 1:40. Fig. 1 shows XRD pattern of sample after mechanical activation and calcination in an inert atmosphere at 800 °C for 30 min

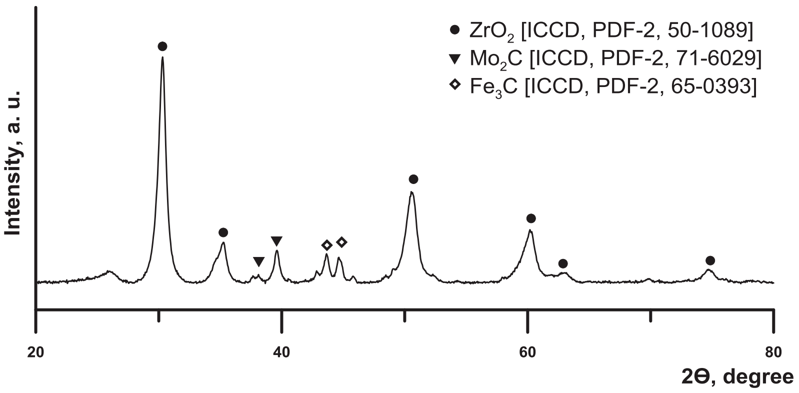

Fig. 1. X-ray diffraction pattern of the carbide-containing composite synthesized by MA and calcined in Ar at 800 °C.

# EFFECT OF THE INTENSIFICATION OF MECHANICAL TREATMENT OF COAL ON THE SLAGGING

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The intense preliminary mechanical processing of fuel is a promising technology in heat-power engineering, which makes it possible to considerably increase the reactivity of fuel. Studies on the production of mechanically activated coal ground in a mill of the disintegrator type and its combustion on fire test benches have been carried out at the Kutateladze Institute of Thermophysics. It is believed that this processing can substantially affect the processes of both mineral matter conversion and slagging.

In experimental studies, Kuznetsk coal was considered after grinding in ball–tube and disintegrator-type mills. The separation of coal dust into fractions according to particle sizes and the X-ray spectral fluorescence analysis of the fractions obtained showed that the coal ground in the ball–tube mill was characterized by an increased concentration of mineral components in the small fraction of standard grinding; this was caused by the predominance of easy to grind minerals containing silicon in them (in the course of grinding, silicon is ground much more rapidly to enrich the small fractions of dust). Crushing in the disintegrator led to the more uniform distribution of the inorganic components of coal over fractions. This was primarily due to the fact that the disintegrator exerts a more intense effect on coal matter and more effectively decomposes organomineral aggregates. Because of this, the small fraction is enriched in elemental calcium, iron-containing minerals, and clay minerals. In this case, fraction of silicon is decreased due to this enrichment of the small fraction. The saturation of small fractions with iron compounds can lead to a decrease in the primary strong ferrous deposits due to the more rapid burning of pyrite and the conversion of iron-containing compounds and thereby reducing the intensity of slagging.

The reported study was funded by RFBR according to the research project № 18-08-01005.

# MECHANOCHEMICAL TRANSFORMATIONS OF POLYMERS DURING FILTRATION IN POROUS MEDIA AND GAP STRUCTURES AS A BASIS OF THE SELECTIVITY OF TECHNOLOGIES FOR LEVELING OF THE INJECTIVITY PROFILE

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Cross-linked macromolecular systems consisting of water, polyacrylamide and organic or inorganic cross-linker, also called hydrogels, are widely used in medicine, water treatment and oil production industry [1, 2]. In contrast to solutions, cross-linked hydrogels possess characteristics of solids, such as a definite physical form and elastic response to tensile and shear strains [3]. When using hydrogels for enhanced oil recovery a composition of chemical reagents with a viscosity similar to viscosity of water is injected into a well so that gellation occurs already in the reservoir conditions. Such systems are sensitive to reservoir conditions and are exposed to various types of breakdown, among which a mechanical breakdown into the porous reservoir plays a crucial role. The effect of the porous media on the hydrogel consists in mechanochemical transformation of a macromolecule, leading to a decrease in molecular weight of polyacrylamide and partial breaking of the cross-links. Destruction of polymer chains by means of mechanocracking is a chemical reaction in which the participating kinetic and structural elements are not individual macromolecules, but an elementary volume of breaking, which is why the mechanical process belongs to the supramolecular level. At the stage of deformation of bonds before the breaking, the reactivity of the system increases with the formation of mechanically excited states and free radicals, which appear as a result of breaking of chemical bonds within the most activated microregions. After filtration through the porous media, the hydrogels create a higher residual resistance factor in large pores, fractures and super reservoirs compared to low-permeability intervals. As a result, the hydrogel injected into the well creates a selective shield in the bottom hole formation zone that diverts injection water into the low-permeability intervals, which were not previously been covered by flooding. This leads to incremental oil production because of the increased formation coverage due to the flooding.

[1] Altunina L.K., Kuvshinov V.A. Russian Chemical Reviews. 76, № 10 (2007) 1034–1052.
[2] Lowman A.M., Peppas N.A. "Hydrogels" in E. Mathiowitz, ed., Encyclopedia of Controlled Drug Delivery. New York: John Wiley & Sons, Inc., 1999. P. 397–418.
[3] Head D.A., Levine A.J., MacKintosh F.C. Phys. Rev. E 68, № 06 (2003) 1.

# ESTIMATION OF THE SPECIFIC SURFACE AREA OF THE FRAME BULK POROUS MATERIAL (WITH/WITHOUT SURFACE NANOLAYER) HAVING STRICT ORDERED GEOMETRICAL PARAMETERS

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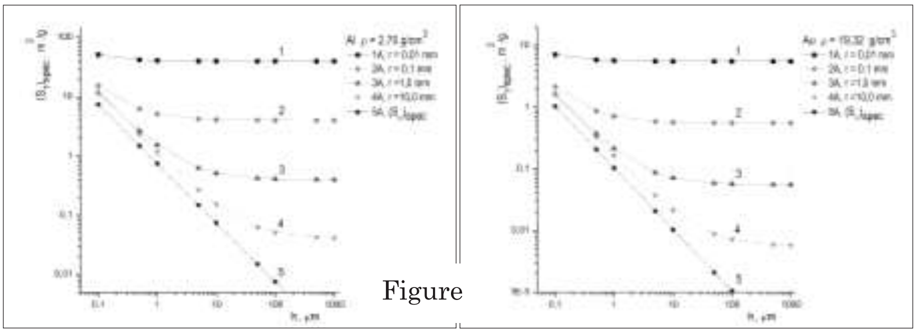
The one/multi component frame bulk porous material with holes uniformly allocated on all surface is considered. Frame material may be useful in chemical/electrochemical processes with participation of the gaseous compounds and requires the gas/liquid permeability. The substantial surface area may be available for reaction (catalytic, electrochemichal or others); it may be achieved also the better material properties (corrosion resistance, mechanical stability and others); modification can be realized by precise physical/chemical methods (laser technology, lithography or others). It was calculated [1] that the specific surface area with equidistant cylindrical holes (radius r, thickness h and density ρ) net is equal (Eq. 1, **Fig.1**): $(S_1)_{spec} = 2/\rho*[1/h + (\pi/(9 - \pi))/r] \sim 2/\rho*(1/h + 0.536/r)$. The relation of the specific surface area of the material with equidistant cylindrical holes net to the initial specific surface area of the material without holes is expressed Eq. 2: $(S_1)_{spec}/(S_{in})_{spec} = 1 + \pi/(9 - \pi)*h/r \sim 1 + 0.536\ h/r$. The frame bulk porous material with deposited submonolayer/monolayer/multilayer is described by Eq. 3: $(S_1)_d/S_{in} = S_1/S_{in} *(1 + \pi*Nd)$, where $(S_1)_d/S_{in}$ is the relation of the result surface area of the bulk porous material with nanolayer to the initial surface area of the material without holes and nanolayer (**Fig. 1 a, b)**; $S_1/S_{in}$ - the relation of the result surface area of the bulk porous material without nanolayer to the initial material surface area without holes and nanolayer; $N_d$ – monolayers number. If the particles in the layer occupy the part D of the material surface area then the relation $(S_1)_d/S_{in}$ is expressed in (Eq. 4):



Figure

$(S_1)_d/S_{in} = S_1/S_{in} * (1 + 4D)$; $(S_1)_d/S_{in} = S_1/S_{in} * 1.4$, for D = 0.1; $(S_1)_d/S_{in} = S_1/S_{in} * 1.8$, for D = 0.2; $(S_1)_d/S_{in} = S_1/S_{in} * 2.6$, for D = 0.4; $(S_1)_d/S_{in} = S_1/S_{in} * 3.4$ for D = 0.6.

[1] Sidelnikova O.N., Zacharov M.A., Salanov A.N. Patent RF № 2336370 (2008).

# HIGHLY CONCENTRATED BINDING SUSPENSIONS AS A CONVENIENT WAY OF SHAPING MECHANOCHEMICALLY SYNTHESIZED CERAMIC MATERIALS.

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After mechanochemical synthesis of ceramic phases, they are to be shaped as the final product. For this purpose, moulding from highly concentrated binding suspensions (HCBS) may be used successfully. The advantages of this method are:

- the constancy of the chemical composition of resulting ceramics, because only water is used as an additional component, and it is removed during drying and sintering;
- low shrinkage, 5-6% as average;
- the strength increased by 20-50% in comparison with the traditional moulding methods;
- the possibility to shape the products with complicated geometry;
- the possibility and convenience to fabricate piece products and small series.

The fabrication technology includes the following stages:

- dry milling of the initial ceramic phase to particle size less than 1 mm;
- wet multistage milling in a ball mill to obtain a suspension with the humidity 12-25%, depending on the ionic potential of the ceramic phase;
- stabilization in the ball mill without milling bodies to achieve maximal fluidizing;
- moulding of the suspension into the semi-finished products using one of the methods;
- drying, sintering.

The following methods are used to obtain a solid semi-product from the liquid suspension:

- centrifugal moulding either for cylindrical or for flat products;
- moulding into gypsum moulds;
- electrophoresis;
- cryogenic moulding;
- moulding on the filler according to the ceramoconcrete technology

Using the indicated method, we studied the technological possibility to obtain the suspension and to carry out subsequent moulding of the following ceramic materials: cordierite, diopside, perlite, diopside porcelain. The stable emergence to positive results with these materials allows us to assume that this method may be used to fabricate final products for the majority of ceramic materials synthesized by means of mechanochemistry.

# IMPROVING OF EUTECTIC STRUCTURES AND STRENGTH PROPERTY OF HT250 GRAY CAST IRON WITH MODIFIED FINE SiC PARTICLES

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The effects of modified fine SiC particles on the strengthening of HT250 gray cast iron with different additions of 0.00, 0.05, 0.10, 0.15 and 0.20 wt% have been investigated at the actual production site.

The results showed that with increasing of SiC particle additions from 0.00 wt% to 0.20 wt%, the tensile strength increased from 4.0% to 18.0% as shown in Fig.1; the microstructures have been refined and the eutectic group increased obviously as shown in Figs 2 and 3. The relationship between grain sizes and tensile strength coincide with the Hall-Petch relationship. It indicates that the reason for the increase in strength is mainly due to the dual effect of micro-structural refinement and eutectic group increscent, which caused by the additions of SiC particles.

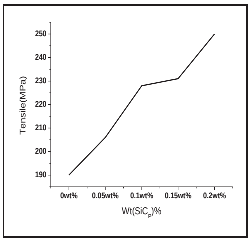

Fig.1

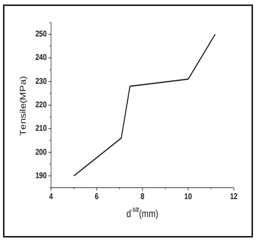

Fig.2

Fig.3

Fig.1 Tensile strength of gray cast iron with different contents of modified fine SiC particles.

Fig.2 The relationship between the diameter and tensile strength of gray cast iron with different contents of modified fine SiC particles.

Fig.3 The eutectic group structures were improved by the addition of the modified SiC powder. (a) 0.0 wt %; (b) 0.1 wt%; (c) 0.2 wt%.

The fine SiC particles can provide enhancements in forming crystallization nucleus and then refining the micro-structures by two ways: firstly, they can form the nucleus themselves; secondly, they can produce nucleus by decomposing and forming very fine non-equilibrium graphite and other silicate particles during crystallization at certain temperatures.

# MODIFICATION OF GRAY CAST IRON WITH EFFECTIVE COMPOSITIONS PRODUCED BY MECHANOCHEMICAL METHOD

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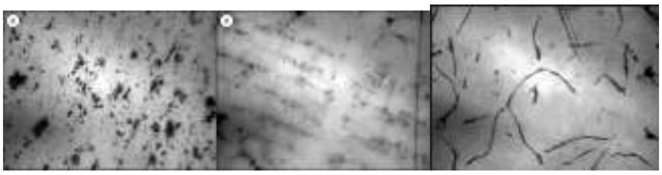
The problem of producing of the modifiers, uniformly distributed in a metal matrix, based on refractory ultradisperse particles wetted by a melt and the problem of obtaining stable results of modification are the object of close attention of many researchers. Mechanochemical treatment (MT) in planetary activators allows not only to grind the material, but also to activate powder particles, and the additional cladding of particles allows to produce modifiers that are well wetted by melts. In addition, mechanochemistry can influence different synthesis processes. The mixtures of nanodisperse tungsten and titanium carbides were synthesized using the method of self-propagating high-temperature synthesis (SHS) combined with MT, and then with the use of MT – the modifiers of composition ($W_2C$, WC, TiC): Me (where Me–Co, Cr, Cu, Fe, Ni , Zr). To conduct a comprehensive comparative analysis of some modifiers for out-of-furnace treatment of cast iron, the modifiers produced by different methods (plasmachemical, coal thermal, mechanochemical, SHS, combined methods, as well as modifiers commercially available) were used. In the experiments on the out-of-furnace modification of gray cast iron the developed compositions showed the greatest efficiency in comparison with the other investigated modifiers. Microstructural studies have established that modifiers affect the phase relationship (ferrite ÷ perlite) – increase the pearlite component; change the shape, length and distribution of graphite inclusions (change the plate graphite to a more compact one); within the limits of ceramic phase concentrations of 0.01-0.2%, the increase of tensile strength was up to 30%, hardness – up to 13%, wear resistance – up to 69%, corrosion resistance – by 2.6 times. It has been shown that when studying the processes of out-of-furnace modification, it is necessary to take into account not only the concentration and composition of the modifiers, but also various technological parameters (design, volume of the mold, method of introducing modifiers, etc.).



(x 400)

**Modification ($W_2C$-WC-TiC, 0.03%):**

**1) in the mold; 2) in the ladle; 3) without modifier**

# ABOUT TWO REGIMES OF MECHANICAL ACTIVATION

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It was established in the studies of mechanochemical decomposition of the nitrates of alkali metals that the yield of decomposition products has an extremal nature. It reaches its maximal value after treatment for a definite time interval, and then decreases to reach a constant value, that is, an equilibrium between nitrite formation and its oxidation into nitrate is established [1]. It turned out that the indicated phenomenon is common also for other mechanochemical processes.

Thus, for zinc ferrite $ZnFe_2O_4$ as example, we successfully followed the changes of specific surface and the parameter characteristic of the activated state. The latter was the change of the quadrupole splitting in the Mössbauer spectra of ferrite. Depending on activation time, its change exhibits a clearly pronounced stage-by-stage character. At the first stage, it varies insignificantly. This corresponds to the stage of progressive decrease in particle size. At the second stage, a rapid increase in quadrupole splitting is observed, along with the start of the formation of activated particles. During this process, splitting remains unchanged.

The reason of aggregation is the transition of the substance into the plastic flow state. The transition into this state also explains the acceleration of chemical interaction between the solid substances, which was observed during the mechanical activation of the mixture: $BaCO_3+WO_3 = BaWO_4+CO_2$ with an increase in the mechanical energy of the apparatus. It follows from the presented data that the activation of solids requires the conditions under which the plastic flow of the material would be achieved as soon as possible. This may be achieved either through an increase in the mechanical parameters (loading rate, an increase in the power of the apparatus etc.) or by using initial smaller particles, which may immediately pass into the plastic flow state during activation.

[1] Avvakumov E.G. Mechanical methods of the activation of chemical processes. 2nd edition. Novosibirsk: Nauka, 1986.

# WAVE MODEL OF ENERGY TRANSFORMATION IN MECHANOCHEMICAL PROCESSES

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Based on the experimental data obtained during indentation of apatite and quartz single crystals as well as mechanical activation and synthesis of these compounds in a planetary ball mill, a wave model of energy transformation from mechanical into chemical was proposed. Simulation of the mechanical activation processes was carried out by applying scratches (grooves) on the surface of apatite and quartz single crystals by the Vickers diamond pyramid, which is usually used when determining microhardness by sclerometry. The stresses in vertical and horizontal sections of scratches were calculated from the values of microhardness according to the Hertz theory, which made it possible to determine the nature of structural disturbances as a function of stress. The indentation zones were studied by scanning electron microscopy, and the powder extracted from the grooves of the scratches was studied by high-resolution transmission electron microscopy. Investigations of vertical scratch zones detected a clear boundary between the process of grinding of a substance and its structural transformation. This boundary is formed when the mechanical stress is equal to the theoretical strength of the substance. Upon dynamic mechanical impact that causes a stress exceeding the theoretical strength of the substance, the energy supplied to the solid is propagated in the form of a strong plastic or "shock" wave. In this case, the excitation of chemical bond vibrations corresponding to the level of the supplied energy occurs. Self-organization of the structure, phase and chemical transformations occur directly in the region of passage/interaction of strong plastic waves of compression and unloading and/or interaction of these waves with those generated by the solid itself at stresses above its theoretical strength. The dynamics of strong plastic waves and the transport of the material mass are determined by the direction of the applied forces and the sliding and/or twinning systems initiated in this case, which depend on the elastic constants of the substance. Mechanochemical synthesis of compounds occurs at the intensity of stress waves reaching the highest value of the theoretical strength of an individual substance in a multicomponent mixture, which causes a highly excited state and self-organization of the entire system. Thus, the applied mechanical energy by wave processes and complex interactions with the lattice and the electronic system of matter is directly converted into the chemical energy.

# NEW INSIGHTS IN BADER’S THEORY

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The chemical behavior of atoms and molecules is entirely defined by the distribution of their electron density. It is by studying the electron density that key concepts of chemical importance come about, such as chemical bonding, reactivity, atomic hybridisation, and the existence of electric multipole moments. The last decades have seen the development of modern theories to study charge density and the most influential to date has been the quantum theory of atoms in molecules (QTAIM), developed by R.W. Bader and colleagues in the 1980s. At the heart of QTAIM there exists the central concept of atomic basins, which subdivides molecule into regions that encase an atomic nucleus: an atom. With the success of Bader’s original theory a series of different topological tools were developed as source function (SF) [eq.1], delocalization indexes, Espinosa indexes, domain-averaged Fermi hole analysis and so on. A novel approach for SF was developed through its calculation from electron densities generated by plane wave (PW) methods. To show the validity of developed method on a series of test systems the results obtained at PW level were compared with those previously obtained through AE methods. Furthermore, a new topological tool is developed, the Bader energy density, $P_{BADER}$ [eq.2], which is introduced and applied to the study case of chemical reactivity *a priori* of $PH_5$.

$$SF(r,\Omega) = -\frac{1}{4\pi}\int_{\Omega} dr' \frac{\nabla^2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \qquad (1)$$

$$P_{BADER}(\Omega) = \frac{E(\Omega)}{V(\Omega)} \qquad (2)$$

# CHARGING ACTIVITY OF MECHANICALLY ACTIVATED PARTICLES

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The application of the mechanochemical activation (MA) method allows reactions to be carried out on the surfaces of inert materials that do not interact with polymer materials under normal conditions. In the course of mechanochemical activation, polymer molecules are degraded to form active radical groups that can interact with hydroxy groups of silicates to form composite particles of different dispersed composition, including those located in the nanometer range. The structure of these particles is a layered composite in which the radical groups of polymeric materials at the molecular level are chemically bonded to the carrier metal silicates. A number of studies have previously shown the interaction of polymeric materials with layered silicates, including mechanoactivation, in which it is assumed that there is an interrelation between the shape (the habitus) of the particle and the charge acivity, of the nanocomposite particles produced. The purpose of this work is to study the charge activity of nanocomposite particles based on silicates, metal oxides and composite particles based on them. As the object of research, mechanically activated particles based on ultra disperse SiO2 with the following composition were taken: α-quartz, $Al_2O_3 \leq 1.6\%$, $Fe_2O_3 \leq 0.6\%$, CaO≤1%, Ni ~ 11 g / t, Cu ~ 7.7 g / t, Ti≤120 g / t, Mn ~ 51g / t, Ba ~ 65g / t, Zr ~ 12g / t, B ~ 97g / t. Joint mechanical activation of silicate particles with polymeric materials, such as polyethylene, sevilene, polyamide, was carried out. Mechanoactivation was carried out in a planetary ball mill (AGO-2) for 30 seconds at acceleration of 60 g. Charge activity of nanocomposite particles was carried out by estimating the intensity of currents in a given temperature range with the use of the ST-1 TST analysis unit manufactured by ODO Microtestmashiny (Belarus). Thus, the calculation of the main parameters determining the charge activity of dispersed particles, including those after mechanoactivation, is carried out. It is shown that mechanoactivation increases the charge activity of dispersed particles of inorganic nature, which makes this type of energy effect promising for obtaining nanoscale and nanophase modifiers of polymer matrices. It is possible to use as a modifier of polymeric materials the metal oxide particles (wastes of metallurgical production) since these particles are characterized by high values of the residual charge and relaxation time.

# INFLUENCE OF PRELIMINARY MECHANICAL TREATMENT, HETEROGENEOUS CATALYTIC ADDITIVES AND IONISING RADIATION ON THERMAL DECOMPOSITION OF POTASSIUM PERSULPHATE $K_2S_2O_8$

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Potassium persulphate ($K_2S_2O_8$) characterized by strong oxidizing property and as oxidizer and the initiator of $K_2S_2O_8$ finds very various application in the industry and laboratory practice. Potassium persulphate is also a convenient model object for studying of decomposition of the inorganic substances containing symmetric covalent bonds and decaying on multistage mechanisms. Besides, $K_2S_2O_8$ easily forms stable radicals during the machining and radiation which remain in a crystal lattice in decades and can enter chemical transformations with other connections when mechanical treated. Therefore, potassium persulphate is perspective substance for solid-phase synthesis and receiving new materials. Earlier it has proposed that $K_2S_2O_8$ decays at 180 – 210°C, or at 180 – 190°C depending on conditions according to the following equation

$$K_2S_2O_8 = K_2S_2O_7 + \frac{1}{2} O_2$$

For a low-temperature stage the catalytic mechanism of decomposition with participation of vapors of water has been offered, and high-temperature decomposition happens on the radical mechanism. In the current work it has been shown that radiation by electrons of $K_2S_2O_8$ leads to forming of radicals and the subsequent thermal decomposition proceeds at temperatures at 20 - 40°C less, than initial substance. The value of decrease of decomposition temperature depends on dose of radiation. Heterogeneous additives, such as $CuSO_4{\cdot}5H_2O$ and $Y_2(C_2O_4)_3{\cdot}10H_2O$ lead to decomposition of $K_2S_2O_8$ at a temperature of 225°C and 240°C, respectively. At these temperatures release of water when heating crystalline hydrates is the reason of course of reaction. Dehydration of both crystalline hydrates occurs in steps, before and after 210°C. Water emitted before 210°C doesn't lead to decomposition of $K_2S_2O_8$, whereas in contrast, the water which emitted from crystalline hydrates at more high temperature initiates reaction of decomposition of $K_2S_2O_8$.

# THE INFLUENCE OF SEPARATE MECHANICAL ACTIVATION ON THERMAL EXPLOSION IN THE POWDER MIXTURE OF NIOBIUM-SILICON

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Joint mechanical activation (MA) of Nb and Si powders has shown [1] that stable layer-by-layer SHS has been attained after 0.5–2.0 min of MA in a planetary mill. Such a MA time was sufficient for formation of $NbSi_2$, $Nb_5Si_2$, and $Nb_5Si_3$ in reactive mixture and attaining good contact between reagents in the layered agglomerates and stable frontal SHS combustion of activated mixtures in an SHS mode. It is interesting to know that it has a decisive importance for the occurrence of combustion.

MA was done in a water-cooled planetary mill (60 g, steel vial and steel balls 5 mm in diameter, mill/ball ratio 1 : 20) under Ar. The separate MA of niobium was carried out in gasoline and then dried in Ar flow. The Nb–Si mixtures containing 62.3 wt % of separately activated Nb and 37.7 wt % of separately activated Si (corresponding to NbSi2 as a combustion product) were manually intermixed (in air) in a mortar for 5 min until visual homogeneity. No mechanochemical formation of silicides in the above mixtures was observed in control XRD measurements (DRON-2 diffractometer). Separately activated mixtures were ignited under Ar in a constant-pressure bomb.

The study found that the layer-by-layer mode of SHS can be realized only after a separate MA of silicon and niobium within 15 seconds. The combustion behavior of separately MA powders is different from jointly activated by a non-stationary mode.

Conducted research on the effect of separate MA of niobium and silicon have shown that the presence of mechanically synthesized silicides of niobium is not a major factor affecting the implementation of the SHS. But the presence of mechanically synthesized phases has an impact on the nature and parameters of combustion.

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# MULTILAYERED Me-Al BASED COMPOSITES OBTAINED BY MECHANICAL ACTIVATION AND SUBSEQUENT CONSOLIDATION BY TORSION UNDER PRESSURE

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Multilayered metal composites are of great interest, both from the point of view of the formation of unique nanostructured states and the complex of acquired physicomechanical properties. To date, the possibility of obtaining multilayer nanolaminates on a variety of metal systems has been demonstrated, the initial components of which can differ substantially in strength characteristics, mutual solubility, melting points and chemical affinity.

In this paper, multilayer nanocomposites based on Me-Al systems (where Me = Cu, Ni, Nb) were obtained using combined deformation processing, including preliminary mechanical activation and subsequent consolidation by torsion under pressure. The comparative study of the influence of the duration of preliminary mechanical activation on the parameters of their microstructure and microhardness values was carried out using X-ray diffraction analysis, scanning and transmission electron microscopy.

The nanocomposites obtained after consolidation of the powder mixtures are characterized by alternating bands of Me and Al, which propagate parallel to the plane of the anvils. The width of the bands separated by interphase and grain boundaries is in the range from 3 to 30 nm. It has been established that microhardness values of the resulting multilayer nanocomposites depend significantly both on the type of the consolidated powders system and on the duration of the preliminary mechanical activation.

This work was performed within the frame of the Fundamental Research Program of the State Academies of Sciences for 2013-2020, line of research III.23. The investigations were conducted using the equipment of Tomsk Material Science Center of Collective Use of Tomsk State University.

# FEATURES OF MICROSTRUCTURE AND MICROHARDNESS OF MULTICOMPONENT PRECURSORS BASED ON REFRACTORY METALS POWDERS AFTER MECHANICAL ACTIVATION OF DIFFERENT DURATION

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The effect of the duration of mechanical activation in high energy (40 g) planetary ball mills (AGO-2) on the morphology changes, microstructure features and microhardness of multicomponent precursors based on refractory metal powders was studied. A compound of W-Cr-Mo-Zr-Ti-Ta-Nb components taken in equal weight parts was used. The duration of mechanical activation under argon atmosphere was 1, 3.5, 5.5, 7.5, 9.5, 11.5, 13.5 and 15.5 minutes.

It has been established that, during the initial stages of treatment, the processes of mixing of the original components are activated, but the precursor being formed is not homogeneous. Against the background of the powder mixture, large (up to 500 μm) and small (no more than 100 μm) plate-like conglomerates are formed.

At the later stages of mechanical activation, the mixture becomes more homogeneous, besides the grinding of large conglomerates up to 100 or less microns, the beginning of processes of their ovalization is observed.

A consequence of high structural and morphological heterogeneity is a significant spread (from 0.5 GPa to 7 GPa) of the microhardness values of the resulting precursors, which is observed at different stages of processing.

This work was performed within the frame of the Fundamental Research Program of the State Academies of Sciences for 2013-2020, line of research III.23. The investigations were conducted using the equipment of Tomsk Material Science Center of Collective Use of Tomsk State University.

# THE INFLUENCE OF A- AND B-CATION SUBSTITUTION ON ELECTRONIC STRUCTURE OF $SrFeO_3$ AND $SrCoO_3$

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Oxides with perovskite structure $SrFeO_3$ $SrCoO_3$ are ancestors of wide range technologically important substances. Representatives of this class of substances are used in high-temperature electrochemical devices, such as oxygen separators and fuel cells. Complex oxides based on them, including those obtained by mechanochemical method, have a number of properties interesting from technological and fundamental point of view.

Previously we use the substitution of the cations in the B positions by high-charge ions $Mo^{6+}$ $W^{6+}$ $Ta^{5+}$ $Nb^{5+}$ to modify the properties of oxygen-deficient oxides of the class described above. Doping with these elements suppressed phase transitions in oxides based on cobalt-ferrite strontium-barium, reduced the size of nanodomains and rise chemical and structure stability of these oxides.

Now we performed the theoretical study of the influence of A- and B- substitution on electronic structure of $SrFeO_3$ and $SrCoO_3$ in the order to clarify how the doping by high-charge cations affects the properties and electronic structure of oxides.

The ab initio calculations in the density functional theory approach was performed with VASP code for various oxides, based on A- and B- cation substituted $SrFeO_3$ and $SrCoO_3$ perovskites. The initial supercell was formed from 2x2x2 elementary cells, in which one of A or B cations was replaced by Ca, Bi, Ba, La, Y (A position) or by Co, Cr, Cu, Zn, Mn. Ni, Ti, V, Ta, Nb, Mo, W (B position). Charges of ions were calculated with Bader code after structure relaxation and electronic structure self-consistent fitting to ground state. It was shown that A-dopants in all cases (even in case of formal oxidation state of 3+) have charges not higher than +2.0e, B-dopants (even for W and Mo with formal oxidation state of 6+) not higher than +2.6e. The electronic structure of valence band keeps their general shape in all cases, not changing significantly after doping. We observe just a shift of Fermi level for different dopants. The dimensions of elementary cell show more valuable variations. The main impact of doping is local change of crystal structure – changes in ionic radius and charges of ions cause difference in local energy of crystal structure. In the case of relatively high charged ions like W, Mo, Ta, Nb it causes significant lowering the local energy and hardening elastic properties, freezing possible structure changes (formation of domain, clustering of oxygen vacations).

# IMPACT OF THE MESOPOROUS MATRIX ON THE THERMAL DECOMPOSITION OF IRON(III) OXALATE

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Mesoporous iron-containing silica nanocomposites is one of the most interesting type of objects which are suitable for considering applications. Thermolysis of iron(III) oxalate (whatever in oxidizing or inert media) is known to proceed through intermediate iron(II) oxalate formation, which is a widely used precursor for nanosized iron oxide particles. This fact allows us to apply the divalent salt thermolysis results to the analysis of trivalent salt transformations. Thermal decomposition of the both compounds is accompanied by significant changes in crystal lattice volume, contributing to the accumulation of mechanical stresses and leading to formation of a product with particle size down to a few nanometers. Ferric oxalate, as opposed to ferrous salt, is water-soluble, and this fact makes it possible to obtain nanocomposites based on mesoporous materials simply by impregnating a matrix with an iron(III) oxalate aqueous solution, followed by a thermal treatment. The usage of porous materials as the matrices for iron oxide nanoparticles stabilization enables us to control their size and shape as well as to protect them from being affected by the external environment. Since the thermolysis of the precursor occurs inside the pores acting as nanoreactors, the substance conversions observed differ from the case of free iron(III) oxalate or have other temperature limits. It does not also exclude the possibility of interactions between the matrix and filling compound.

The present study is dedicated to thermolysis of bulk ferric oxalate and the substance embedded into SBA-15 mesoporous silica with the typical hexagonal quasi-ordered porous system under both inert and oxidative conditions. We have simultaneously observed two different ferric oxalate forms located within the pores and on the external surface of silica. Synchronous thermal analysis showed the evident difference in their behavior during the decomposition process. The initial objects and the products were analyzed by X-ray powder diffraction and Mossbauer spectroscopy.

# MECHANOSYNTHESIS OF MAGNETO-ABRASIVE POWDER COMPOSITES IN THE EXOTHERMIC MIXTURES $Fe_2O_3$-Fe-Me

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Magnetic abrasive machining (MAM) is one of the advanced finishing processes producing a high quality level of any type surface (cylindrical, flat, spherical, helical, curved body surfaces etc.) for different kinds of materials (glass, metals, ceramics, complex alloys, etc.). MAM technology provides a thin surface roughness up to the range of nanometers and a simultaneous increase of surface quality with a reduced defect concentration. Magnetic and abrasive properties of the working media are determining the productivity of the finishing process and the quality of the treated surfaces. The intensive mechanical treatment of powdered mixtures in exothermically reacting ($Fe_2O_3$:Fe:*Me*, *Me* = Al, Zr) systems in high-energy planetary ball mills is performed to synthesize effective magneto-abrasive composites with the particle size range of 1-100 μm. X-ray diffraction, scanning electron-microscopy, Mössbauer spectroscopy and investigations of mechanical properties accompanied by the measurements of the abrasive activity in the finishing process of the surface polishing are used for the characterization of the as-prepared composites.

The promising point is the use of pre-synthesized mechanocomposites of active metals as precursors, which facilitates the production of the final composite particles in a narrow dimensional range with a uniform distribution of abrasive particles.

It is shown that the formation of composites is the result of intensive processes of grinding and deformation which contributes to intensified redox reactions (mechanochemical synthesis) leading to the formation of abrasive particles ($Me_xO_y$) in iron matrix. The main parameters and mechanisms of the formation of the optimal structure of composites are revealed. It is demonstrated that the smallest roughness of the machined surface ($R_a \sim 1$ nm) is achieved in the case of using the mechanosynthesized Fe/$ZrO_2$ composite.

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# MECHANOCHEMICAL INTERACTION IN Fe-Ga-In SYSTEM

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Systems Fe-Ga, Fe-In, Fe-In-Ga and other are interesting regarding their magnetic properties. Fe-Ga alloys are well known because of the magnetostriction effect. These alloys are promising materials for applications as components of composites, for example, in the sensors and actuator technology.

The mechanochemical interaction of powder Fe with liquid Ga-In eutectic was studied. Systems Fe-Ga and Fe-In were previously investigated. Mechanochemical synthesis was performed in high energy ball mill. The products of mechanochemical synthesis were studied by Mössbauer spectroscopy, X-Ray diffraction (XRD) and transmission electron microscopy (TEM).

Comparative study of mechanical alloying in Fe-Ga-In with respect to Fe-Ga and Fe-In systems has allowed us to observe various behavior of examined samples. The idea of introduction of liquid eutectic proved to be correct, and further adjustment of Ga-to-In ratio in order to stabilize certain kind of crystal chemical and magnetic ordering could be required. It is evident that indium addition, even in relatively low quantities required for eutectic formation, suppresses intermetallics formation to a notable extent, at least on a local scale, and favors formation of the $D0_3$-type order. While it is still an open question, whether it is possible to stabilize the composition around technologically important 19 at. % of Ga, it was proven that mutual immiscibility of Fe and In could be overcome using mechanochemical approach.

# MECHANOCHEMICAL SYNTHESIS OF APATITE AND OTHER CALCIUM ORTHOPHOSPHATES AS MATERIALS FOR MEDICAL PURPOSES

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Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and calcium orthophosphates $\beta$-$Ca_3(PO_4)_2$, $\alpha$-$Ca_3(PO_4)_2$, and $Ca_4(PO_4)_2O$ are widely used in medicine [1]. The structure of apatite allows for a wide range of substitutes: ions significantly differing in their diameter and valence from those of ions contained in apatite can acts as substitutes. Substitution affects physical, chemical and biological properties of apatite: its bactericidal action, resorption rate in biological fluids and implantation rate of implants containing substituted apatite.

By the mechanochemical method, we synthesized varieties of apatite containing cations with different ionic radii ($Mg^{2+}$, $Zn^{2+}$, $Ba^{2+}$) and different valences ($La^{3+}$, $Na^{+}$, $Cs^{+}$) substituting for $Ca^{2+}$. In the case of cations with different valences, charge compensation occurs by formation of OH-group vacancies or by substitution of oxygen ion $O^{2-}$ for OH-group. We found that coordination of complex anions plays an important role in the formation of substituted apatite. The phosphate group in apatite has tetrahedral coordination, and is easily replaced by the silicate group with tetrahedral coordination despite the heteroionic substitution: $SiO_4^{4-}$ + Vacancy → $PO_4^{3-}$ + $OH^{-}$. As a result, a vacancy in the position of the hydroxyl group is created to compensate the charge. In heteroionic anionic and cationic double substitution of silicate for phosphate and lanthanum for calcium, complete substitution is possible to form lanthanum silicate with an apatite structure. The phosphate group replacement by complex anions with predominantly octahedral coordination is much more difficult; in particular, the aluminate and zirconate substitution, which does not exceed 0.5 mol. The limits of substitution in the cation and anion sublattices of the mechanochemically synthesized varieties of apatite, the optimal synthesis conditions of substituted apatite and high-temperature forms of calcium orthophosphates will be presented.

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# CRYSTAL STRUCTURE OF LANTANUM-SILICATE CO-SUBSTITUTED APATITE OBTAINED BY MECHANOCHEMICAL SYNTHESIS

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Hydroxyapatite is widely used in various fields of medicine: as coatings for implants, bioresorbable ceramics, fillers of bone defects. The structure of hydroxyapatite allows a wide range of substitutions, both in the cation sublattice and in the anionic sublattice. Substitutions occurring in the structure of hydroxyapatite change its physico-chemical and biological properties, which allows to expand the scope of its use.

This work is devoted to the study of the structure and thermal stability of lanthanum-silicate co-substituted apatites obtained by the mechanochemical synthesis in AGO-2 planetary ball mill.

X-ray phase analysis showed a significant decrease of the crystallite size for unsubstituted hydroxyapatite at a temperature of 1300 ˚C, as well as decomposition into α-tricalcium phosphate and calcium oxide at 1400 ˚C. For the two-co-substituted-lanthanum-silicate apatite, in addition to the main phase, silicocarnotite reflexes are observed starting from 1200 ˚C. Four- and six-co-substituted-lanthanum-silicate apatites are stable up to a temperature of 1400 ˚C.

Refinement of the structure of the six-co-substituted-lanthanum-silicate apatite by the full-profile Rietveld method showed that lanthanum ions replace calcium ions in both positions (Ca1 and Ca2). Lanthanum ions located in the position of Ca1 are localized without displacement, while those in the Ca2 position are shifted toward the oxygen ion located on the *c* axis. The concentration of lanthanum ions in the position of La2 is about 2 times greater than the concentration in La1.

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# MECHANOCHEMICAL REDUCTION OF $GeO_2$ AND $SiO_2$ TO OBTAIN HIGHLY DISPERSED SILICON AND GERMANIUM

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Ultra-disperse germanium and silicon powders are used in the coating of optical components, as doping additives, in the creation of new composite materials, nanotechnologies, microelectronics, microwave devices, fiber and infrared optics, nuclear physics (gamma-ray detectors). The possibilities of its application are expanding every year.

The thermodynamic possibility of reactions of magnesium with oxides of germanium or silicon was determined basing on literature data. The physico-chemical properties of silicon, germanium, magnesium and their oxides (melting points, redox potentials, interaction with acids, etc.) prevent the sintering of products of mechanochemical reduction and allow the formation of Si(Ge)/MgO mechanocomposites. Magnesium oxide reacting with hydrochloric acid forms a highly soluble compound $MgCl_2$, which can be extracted quite easily from Si(Ge)/MgO mechanocomposites. Due to the fact that the reduced germanium and silicon do not react with the diluted solution of a hydrochloric acid it is possible to separate silicon and germanium from by-products of mechanochemical reduction by acid treatment.

The effect of the stoichiometric composition and the time of mechanical activation on the composition of the products of mechanochemical reduction of $GeO_2$ or $SiO_2$ by magnesium were studied by X-ray phase analysis. It is shown that the process of mechanochemical reduction is completed by 4 min of activation. The conditions for separating germanium and silicon from mechanocomposites are determined. Electron microscopic analysis showed, that ultra disperse germanium and silicon powders consist of aggregates of primary particles, almost spherical in shape with sizes from 50 to 100 nm. The energy-dispersive X-ray spectroscopy (EDS) method was used to determine the magnesium content in the obtained of silicon and germanium powders.

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# SYNTHESIS OF MOLYBDENITE FROM ELEMENTS VIA MASHS

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Molybdenite (two-dimensional molybdenum disulfide $MoS_2$ with few layers) is scientifically and technologically important material. The increased interest in synthesis of $MoS_2$ is caused by its potential applications in areas such as electrochemistry, lubrication, catalysis, and as host material for intercalation chemistry. In [1], $MoS_2$ has been successfully prepared by a method of mechanical activation (MA) of mixture of $MoO_3$ with S, followed by calcination at 600°C for 2 hours. In [2], the work was undertaken with the aim of studying the conditions of $MoS_2$ preparation by self-propagating high-temperature synthesis (SHS) of molybdenum and sulfur powders (the calculated adiabatic combustion temperature of Mo+2S mixture is ~2600°C). However, SHS led to the formation of a two-phase system [3]: $MoS_2$ with a $Mo_2S_3$ impurity. We did the first similar attempt to synthesize $MoS_2$ from elements by SHS with preliminary mechanical activation of reactants mixture (MASHS).

A planetary ball monovial stainless steel mill (Pulverizette 6) was used for MA. Two (Mo+2S) samples of 8.389 g and 13.428 g in weight were processed for 5h and 8 h correspondingly at carrier rotation 210÷600 rpm. The vial (500 cm3 in the volume) filled by 109 balls (each 1 cm in diameter) was used in these experiments. According to XRD, the progress of the reaction was negligible after MA. The processed material showed broadened lines of Mo (PDF Number: 42-1120), while the diffraction lines of sulfur (PDF Number: 83-2285) disappeared due to amorphization and polymerization (glass formation).

At the second stage of the synthesis, the sample was sealed in the double wall quartz ampoule. While heating the ampoule, a very intensive exothermic reaction was observed at ~700°C. The final step of the synthesis was annealing of the material at 1050°C during 2 h. According to XRD the obtained product was single phase $MoS_2$ (PDF Number: 17-44).

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# THE USE OF RAMAN SPECTROSCOPY FOR THE IDENTIFICATION OF SODIUM POLYSULPHIDE OBTAINED BY THE MECHANOCHEMICAL METHOD

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Raman spectroscopy has made remarkable progress in recent years. The synergism that has taken place with the advent of new detectors, Fourier transformation Raman and fiber optics has stimulated renewed interest in the technique. Its use in academia and especially in industry has grown rapidly [1]. Its use in research work in the study of various substances obtained by different methods, is growing rapidly.

In this work, we used a Raman spectrometer with the following parameters:

1) Power - 35 mW, filters ND = 0.5 and ND = 1 were also used, which reduce the intensity by 30% and 10%, respectively;
2) Solid State Laser;
3) Lattice - 1800/500;

Samples of sodium polysulphide were analyzed, which were first obtained mechanochemically, they consisted of sodium hydroxide and elemental sulfur. The difference between experiments on obtaining samples was the time of mechanochemical activation and the ratio of the reacting components.

The Raman spectra decoding results identified peaks of sodium polysulphide with different sulfur contents (S2-8). Comparison of spectra with literature data has proved a possibility of synthesizing of sodium polysulphide by a mechanochemical method.

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# MECHANOCHEMICAL SYNTHESIS OF DOUBLE HYDROXIDES OF TIN AND ALKALI EARTH METALS

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Double hydroxides of tin and alkali earth metals $MSn(OH)_6$, where M = Mg, Ca, Sr, Ba, have strict stoichiometric ratio M/Sn and may be used for preparation of pure alkali earth stannates. As shown recently, double hydroxide $MgSn(OH)_6$ may be easily prepared by sol-gel co-precipitation technique [1], whereas in the cases of compounds of Ca, Sr and Ba application of such method is hindered.

In the present work for preparation of the double hydroxides we have used the solid state interactions in a hand mortar. As starting materials, crystalline $SnCl_4 \cdot 5H_2O$ and alkali earth chlorides $MCl_2$ (M = Mg, Ca, Sr) and $Ba(NO_3)_2$ were taken. The mixtures of chlorides (tin and alkali earth metal) and barium nitrate were homogenized in a mortar. The molar ratio Sn/alkali earth was 1. Resulting burdens were mixed with solid NaOH (molar ratio NaOH/Sn was 6) and the mixture was mechanically treated in a handle mortar for 5 min. After the mechanical treatment the products were washed several times by water, filtered, dried at room temperature for 12 h on air and analyzed by X-ray powder diffraction technique.

According to the X-ray diffraction data, the phase composition of the samples depends on the type of the cation. In case of magnesium and calcium, double hydroxides $MSn(OH)_6$ were synthesized. There was a small impurity of $Mg(OH)_2$ in Mg-Sn sample. Whereas in the case of strontium and barium double oxo-hydroxides form.

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# MECHANOCHEMICAL SYNTHESIS OF NANOCOMPOSITES BASED ON $Fe_3O_4$ AND LAYERED DOUBLE HYDROXIDES

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Layered double hydroxides (LDHs), represented by the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, are a class of ionic lamellar solids with positive charged layers counterbalanced by exchangeable interlayer anions. The layers of LDHs are made up of infinite sheets of edge-sharing metal octahedra, where part of M(II) cations ($Mg^{2+}$, $Co^{2+}$, $Ni^{2+}$) are replaced by M(III) cations ($Al^{3+}$, $Fe^{3+}$, $Cr^{3+}$). Because of the large variety of anions that can be incorporated between the brucite-like layers, the high anionic exchange capacity of these materials, and the large surface area values, LDHs can be successfully used as sorbent materials. Composites of LDHs with magnetic phases ($Fe_3O_4$, $MgFe_2O_4$) provide an opportunity to use magnetic field to separate the sorbents. Conventional synthesis method of magnetic composites with LDHs is the co-precipitation of metal salts from a mixed solution in the presence of a magnetic substrate. This path has significant drawbacks, such as complicating, duration, large amounts of liquid wastes. Mechanochemical method allows avoiding these drawbacks.

In this work we propose “soft” mechanochemical synthesis of the magnetic composites $Fe_3O_4$/LDHs (Mg-Fe(III), Ni-Fe(III), Co-Fe(III)) in a hand mortar using $FeSO_4\cdot 7H_2O$, $FeCl_3\cdot 6H_2O$, $MCl_2\cdot 6H_2O$ (M-Mg, Co, Ni) and NaOH as initial reagents. By this method $Fe_3O_4$ and LDH phases are formed in a reaction volume simultaneously. Mixture of iron salts (for $Fe_3O_4$ synthesis, molar ratio Fe(III)/Fe(II)=2) was homogenized with mixture of $FeCl_3\cdot 6H_2O$ and $MCl_2\cdot 6H_2O$ (for LDH synthesis, molar ratio M/Fe-2, 3 and 4) in a mortar. The resulting molar ratio Fe(III)/Fe(II) was 3. Solid NaOH were added to obtained mixture with intensive grinding for 5 min. The resulting pastes were washed several times by water and dried on air at room temperature. The powder XRD patterns indicate that obtained composites consisted of $Fe_3O_4$ and corresponding LDH phases. Specific surface area was 100-150 $m^2/g$. Obtained materials demonstrated high As (III) sorption capacity. Suggested “soft” mechanochemical synthesis of the magnetic nanocomposites $Fe_3O_4$/LDHs is simple, fast, relatively inexpensive and environmentally more friendly.

# EFFECT OF WATER VAPOR PRESSURE ON THE MECHANOCHEMICAL SYNTHESIS OF GAMMA LITHIUM MONOALUMINATE

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The influence of the partial pressure of water vapor on the phase composition of lithium aluminates formed during the thermal treatment of the initial and mechanically activated mixture of gibbsite and lithium carbonate is investigated. Activation of the mixture was carried out in a planetary mill AGO-2 with a centrifugal acceleration of 40 g for 1-10 minutes. It was found that the phase composition of lithium monoaluminates formed during the thermal treatment of the initial and briefly mechanically activated mixture depends on the partial pressure of the water vapor at which the reaction is carried out. When the process is carried out in the air atmosphere ($P_{H2O}$ = 1200-1300 Pa), α-$LiAlO_2$ is formed. When the mixture is heated in a helium atmosphere ($P_{H2O} \leq 4$ Pa), a mixture of α-$LiAlO_2$ and γ-$LiAlO_2$ is formed. Under conditions of a dynamic vacuum ($P_{H2O} \leq 0.1$ Pa), γ-$LiAlO_2$ is predominantly formed.

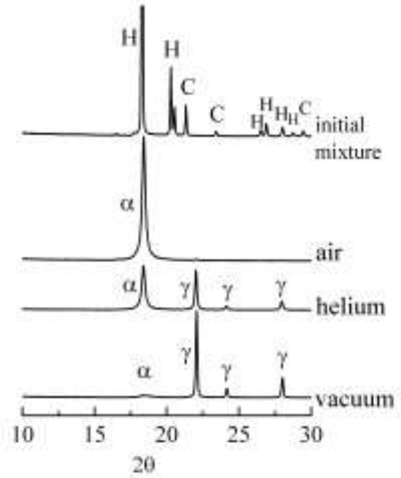

Fig. X-ray diffraction patterns of the initial mixture of gibbsite and lithium carbonate and a mixture heated to 800 °C in air, helium and vacuum. G - $Al(OH)_3$, C - $Li_2CO_3$, α- $LiAlO_2$, γ- γ-$LiAlO_2$. 2θ - Bragg angle.

The phase composition of lithium monoaluminates formed during the thermal treatment of a mechanically activated mixture containing amorphous aluminum hydroxide is independent of the partial pressure of water vapor. In all cases, regardless of the partial pressure of water vapor, a highly dispersed γ-$LiAlO_2$ is formed. The mechanism of influence of partial pressure of water vapor on the phase composition of lithium aluminates is discussed.

The work was performed within the state task of ISSCM SB RAS (project 0301-2018-0006).

# MECHANOCHEMICAL SYNTHESIS OF METAL PHOSPHONATES

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The exploration of metal phosphonates chemistry has gained great interest during the last decades, because of their structural diversity. Transition metal phosphonates are promising candidates for an application as electrocatalysts in oxygen evolution reactions (OER) [1].

Here, we present the in situ investigation of mechanochemical syntheses of different divalent manganese aminophosphonates by synchrotron X-ray diffraction [2]. Nitrilotri(methylenephosphonic acid) and *N*,*N*-Bis(phosphonomethyl)glycine were chosen as ligands. The liquid-assisted milling process can be divided into three steps, including an amorphous stage. One of the products has not been obtained by classical solution chemistry before. The structure of the new material was determined from PXRD data.

These metal phosphonates and/or their derivatives are considered to be active in electrochemical energy conversion [3]. The verification of their applicability is one of the topics of our resent research.

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# THE EFFECT OF MECHANOCHEMICAL SYNTHESIS ON COMPOSITIONAL ORDERING AND DIELECTRIC PROPERTIES OF TERNARY PEROVSKITES

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Ferroelectric ternary perovskite oxides of the $Pb_2B^{3+}B^{5+}O_6$ type, are the components of many functional materials possessing remarkable dielectric, electrostrictive, pyroelectric, and piezoelectric characteristics. Properties of these oxides depend crucially on the ordering degree of $B^{3+}$ and $B^{5+}$ cations. While in the highly-ordered state a sharp ferroelectric or antiferroelectric phase transition takes place, in the disordered state a relaxor state is observed, characterized by a diffuse and frequency-dependent maximum of the dielectric permittivity.

Previously we have found out that the use of mechanochemical synthesis enables one to modify substantially both dielectric and relaxor properties of $Pb_2Fe^{3+}B^{5+}O_6$ ($B^{5+}$ - Nb, Ta) ceramics [1, 2]. In the present study we investigated the effect of the conditions of the mechanochemical synthesis on the structure and dielectric properties of several $Pb_2B^{3+}B^{5+}O_6$ ceramics ($B^{3+}$ - Sc, In, Yb and $B^{5+}$ - Nb, Ta). High-energy mechanical activation was carried out using AGO-2 planetary-centrifugal mill at ball acceleration of 40g.

It was found out that high-energy mechanical activation during mechanochemical synthesis stimulates disordering of $B^{3+}$ and $B^{5+}$ cations in ceramics of the studied $Pb_2B^{3+}B^{5+}O_6$ perovskites. Using mechanochemical synthesis disordered modifications of $Pb_2B^{3+}B^{5+}O_6$ ($B^{3+}$ - In, Yb and $B^{5+}$ - Nb, Ta) were obtained for the first time without the use of any additives. In some cases it is possible to vary within a wide range compositional ordering degree of the $B^{3+}$ and $B^{5+}$ cations and correspondingly both the temperature and diffusion of dielectric permittivity maxima in ceramics by changing the regimes of the mechanochemical synthesis and using the preliminary synthesized $B^{3+}B^{5+}O_4$ precursors.

This study was supported by RFBR project 17-03-01293_a.

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# INTERACTION OF MATERIALS WITH GRAPHITE FOIL DURING SPARK PLASMA SINTERING: CASE STUDIES FOR Ni-W AND YTTRIA-STABILIZED ZIRCONIA POWDERS

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In the practice of Spark Plasma Sintering, consolidation is usually conducted in a graphite die using graphite punches. Graphite foil is used to protect the die and punches from the chemical interaction with the sample during the sintering process. At the same time, graphite foil can act as a source of carbon and its presence can affect the composition of the sintered compact.

The goal of this work was to investigate the influence of graphite foil on the phase composition, microstructure and properties of the sintered materials. A metallic alloy Ni-15at.%W, a mixture of Ni and W powders of the same composition and yttria-stabilized zirconia were chosen as materials for this study. For the preparation of the Ni-W alloy, high-energy mechanical milling was used.

In case of the Ni-W alloy, carbon from the graphite foil diffuses into the bulk of the sample forming WC in the subsurface layer of the sample near the interface with the graphite foil. The carbide particles are mainly found along the boundaries of the initial agglomerates of the mechanically milled powder. In the case of the mechanically milled powder mixture, the inner part of the compact contains particles of $Ni_2W_4C$ in contrast to the compact obtained from a simple Ni+W mixture, in which no carbide phases were detected in the sample's interior.

In the case of partially densified yttria-stabilized zirconia, a change in the sample color from white (powder) to black (sintered compact) indicated that the whole sample volume was affected by the presence of carbon. Structural changes occurring in the material upon its interaction with carbon will be reported in this presentation.

Studies of the Spark Plasma Sintering behavior of yttria-stabilized zirconia powders were supported by RFBR according to research project No. 18-33-00713 mol_a.

# SYNTHESIS AND STUDY OF ELECTRICAL CONDUCTIVITY OF $AL_2O_3$/METAL COMPOSITE MATERIALS

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The possibility of creating dense composite materials of aluminum oxide with metals (W, Fe, Ti, Cr), combining the characteristics of aluminum oxide (chemical resistance, strength, etc.) and the electrically conductive properties of metals was investigated.

Composites were obtained by mixing (grinding in a mortar, mechanical activation) of nano-powder $Al_2O_3$ and metal powders followed by pressing (uniaxial, isostatic) into a briquette and sintering (free sintering in vacuum, HIP). Composites with relative densities in the range of 90 - 98% and the content of the metallic phase (except for W) up to 52% have been obtained. Composites of aluminum oxide with tungsten can not be obtained, due to the chemical interaction of the components. X-ray phase analysis did not reveal the formation of side-phases (intermetallic compounds, spinels, oxides) in $Al_2O_3$/Me (Fe, Ti) composites. It was found that the electrical conductivity of composites with metals (Fe, Ti, Cr) has the character of a percolation transition, that is, composites possess either high resistance $10^9$ - $10^{10}$ Om*m or low resistance $10^0$ - $10^2$ Om*m.

In order to obtain composites with a resistance in the range of $10^3$ - $10^8$ Om*m, an attempt has been made to distribute the metallic phase into layers between grain boundaries and due to the thickness of the layer (cross-sectional area) affect the resistance of the composite.

# EFFECT OF INTENSIVE PLASTIC DEFORMATION ON STRUCTURE AND MAGNETIC PROPERTIES OF $Al_2O_3$/Co(P) NANOCOMPOSITE PARTICLES

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Ceramometals, consisting of uniformly dispersed ferromagnetic metallic particles in an oxide matrix, have been the subject of intensive study due to their unique combination of magnetic and mechanical properties. It was found that the desired mechanical properties (fracture toughness) of bulk cermets can be achieved by introducing Co particles with certain hcp/fcc phase ratio. However, to prepare cermet by traditional mechanochemical synthesis, long time is needed, reaching up to 16-20 hours of treatment in a high energy ball mill.

We report on the evolution of structural and magnetic properties of $Al_2O_3$/Co(P) composite particles under intensive plastic deformation during ball milling process. To prepare starting composite particles, the $Al_2O_3$ granules were coated with a $Co_{95}P_5$ shell by electrolysis plating. We use the core-shell particles as starting powder for mechanochemical synthesis in order to reduce the time needed to prepare the composite particles with optimal hcp/fcc phase ratio. The properties of the composite particles are characterized by scanning electron microscopy, X-ray diffraction, and the magnetic measurement. The ball milled composite powders consist of a mixture of hcp and fcc phases. After 45 minutes of milling the particles were plastically deformed and the volume fraction of superparamagnetic particles significantly increases up to 12 vol%. The magnetic properties of the milled composite particles are correlated with changes in the microstructure. The local magnetic anisotropy field depends on the amount of hcp-Co phase in sample and its value decreases from 8.4 kOe to 3.8 kOe with an increase in milling duration up to 75 minutes. The composite particles after 45 minutes of milling possess a high enough value of ductility necessary to produce a bulk material with the best combination of magnetic and mechanical properties.

# INFLUENCE OF MOISTURE CONTENT ON THE EFFICIENCY OF GRINDING OF PLANT RAW MATERIALS

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It is known that one of the most important parameters responsible for the efficiency of processing and mechanical activation of lignocellulose is moisture content [1-2].

The aim of the present work is to study the dependence of the efficiency of grinding of lignocellulose biomass on the moisture content.

It has been shown that the size and morphology of the product particles depend not only on the intensity of the impact, but also on the moisture content in the material being treated (Fig. 1).

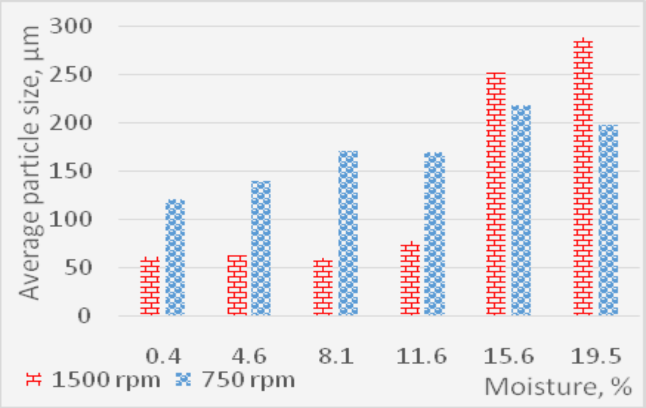

Fig.1. Dependence of the particle size on the raw material moisture at low (750 rpm) and high (1500 rpm) grinding intensity.

At a moisture content of more than 12% in the raw materials, there is a sharp decrease in the grinding efficiency associated with the formation of large aggregates of smaller product particles [3]. It has been shown that for more effective grinding, high-intensity modes of treatment and raw materials with a moisture content of less than 12% should be used.

This work was supported by the Russian Science Foundation (project no. 16-13-10200).

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# MEHANOCHEMICAL MODIFICATION OF NIMESULIDE

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Nimesulide (N) (chemically, 4-nitro-2-phenoxy meth-esulfanilamide) is a relatively new nonsteroidal anti-inflammatory analgesic drug. It is practically insoluble in water (<0.02 mg/ml). The very poor aqueous solubility of the drug may lead to low bioavailability. The objective of the present study was to investigate the possibility of improving the solubility and the bioavailability of N via complexation with polysaccharide arabinogalactan (AG), disodium salt of glycyrrhizic acid ($Na_2GA$), HP-β-cyclodextrin (HP-β-CD), $MgCO_3$. The solid dispersions (SD) have been prepared using mechanochemical technique. The physical properties of Nimesulide SD in solid state were characterized by differential scanning calorimetry, X-ray diffraction studies. The characteristics of the water solutions, which form from obtained solid dispersions were analyzed by reverse phase and gel permeation HPLC. It was shown that solubility of N increases for all complexes under investigation. This phenomenon is explained by complexation with auxiliary substances, which was shown by phase solubility and $^1$H NMR relaxation methods. The PAMPA assay was used for predicting passive intestinal absorption. The enhanced permeation of N across an artificial membrane fabricated from mechanochemically obtained complexes with polysaccharide arabinogalactan (AG), disodium salt of glycyrrhizic acid ($Na_2GA$) and HP-β-cyclodextrin (HP-β-CD) in comparison with that of pure N was observed.

The complexes were examined for anti-inflammatory activity on a model of histamine edema. The substances were administered orally once per day to male albino mice. As a result, it was found that all investigated complexes dose-dependently reduce the degree of inflammation. The best results were obtained for the complexes of Nimesulide with disodium salt of glycyrrhizic acid ($Na_2GA$) and HP-β-cyclodextrin (HP-β-CD). In noted case the inflammation can be diminished up to 2 folds at equal doses of N.

# AN EXAMPLE OF DESTRUCTION OF ANTIDOTE DURING ITS MECHANOCHEMICAL MODIFICATION WITH POLYSACCHARIDE

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To protect the crop from the toxic effects of soil residues of herbicides, antidotes are recommended. Thus, the known antidote Naphthalic Anhydride (NA) promotes the acceleration of the detoxification of herbicides (sulfonylureas) in the soil and the growth of resistance to them.

To improve solubility of NA, we proposed a method for its mechanochemical modification with polysaccharides. The solubility analysis of the obtained NA compositions with polysaccharides showed a real possibility of improving the solubility of NA up to 35-40 times. An abnormally sharp increase in solubility of up to 250-300 times was observed in the composition NA: Na-CMC = 1: 2. This result can be explained by the possibility of hydrolysis of NA to the corresponding dicarbonate (ND, 1,8-naphthalenedicarboxylic acid). This assumption was confirmed by NMR spectroscopy and HPLC analysis. In our opinion, the hydrolysis of NA to ND is possible according to the following scheme: (i) in the beginning, the activation of the C (O) -O-C (O) group of NA takes place due to interaction with Na-CMC under conditions of joint machining.(ii) mehanoactivated composition of NA: Na-CMC = 1: 2 upon entry into the aqueous medium begin to hydrolyze to NA due to the interaction of the active group C (O) -O-C (O) NA with a water.

Biological studies of NA compositions with polysaccharides, as well as a sample of ND, were carried out under conditions of the artificial climate laboratory. Analysis of these data showed that the modification of NA polysaccharides increases its antidote effect on rapeseed, but decreases on corn. Such result can be explained by the fact that polysaccharides affect the penetration of NA.

Thus, the possibility of regulating the antidote properties of NA during its mechanochemical modification with polysaccharides has been demonstrated; the possibility of hydrolysis of NA to the corresponding acid was first established by a joint mechanochemical treatment of NA with Na-CMC polysaccharide; it is shown that ND has stimulating properties on maize seeds, as well as weak antidote activity in soils infected with the herbicide of the sulfonylurea series.

This work was supported by the Russian Foundation for Basic Research (grant No. 15-29-05792).

# BIOLOGICAL ACTIVITY OF MECHANOCOMPOSITES IN THE CULTURE OF PLANT TISSUES *IN VITRO*

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Novel inexpensive regulators of morphogenesis *in vitro* providing active regeneration and rapid reproduction are necessary for the broad use of biotechnological methods in plant cultivation. The biological activity of three mechanocomposites manufactured at the ISSC&M SB RAS on the basis of the humates of brown coal UB09-1 (humate + soda 10 %), UB09-3 (humate + beet cake), UB09-3 (humate + soy flavour) was studied:

The test system of the leaf tissues of spring rape (*Brassica napus* L.) included two stages. At the I stage, the explants of aseptic leaves with the area of 0,5-1 cm$^2$ were placed on the media for callus formation MS with auxin 2,4-D added in the concentration of 1 mg/l (reference). Along with auxin, the mechanocomposites under investigation in the same concentration were added into the experimental media before autoclave treatment. The intensity of callus formation was determined using the 4-number score scale. According to our data, UB09-2 stimulated primary callusogenesis by 50%, while the effect of other preparations was not reliable.

At the II stage, the explants of calluses 0,1 cm$^3$ in volume were subcultures on the media for regeneration MS with the addition of BAP cytokinine (references). Instead of cytokinine, mechanocomposites were added into the experimental media. During the first month of incubation, all the three preparations suppressed the growth of callus tissue, but during the second month the volume of callus on the medium with UB09-3 increased nearly by a factor of 3.

Mechanocomposites demonstrated the ability to induce differentiation (cytokinic activity), though less than cytokinine BAP in the same concentration. During the first month, the frequency of regeneration on the media with UB09-1 was observed to be 15%, with UB09-3 – 10%, while regeneration was absent in the case with UB09-2. During the second month, the frequency of regeneration on the media with UB09-1 and UB09-3 increased to 30 and 35%, respectively, while on the medium with UB09-2 it reached 11%. Rhizogenesis on the media with mechanocomposites for 2 months reached 100% purity.

Thus, the stimulating action of mechanocomposites on the development of callus, shouts and roots in the culture of plant tissues was proven. The effect depends on the composition of the preparation.

# EXTRACTION OF ANTHRAQUINONES FROM *CASSIA OCCIDENTALIS L.* BY MECHANOCHEMISTY AND EVALUATION ANTI-INFLAMMATION EFFECTS BY OVALBUMIN-INDUCED AIRWAYS INFLAMMATION IN A MOUSE MODEL OF ALLERGIC ASTHMA

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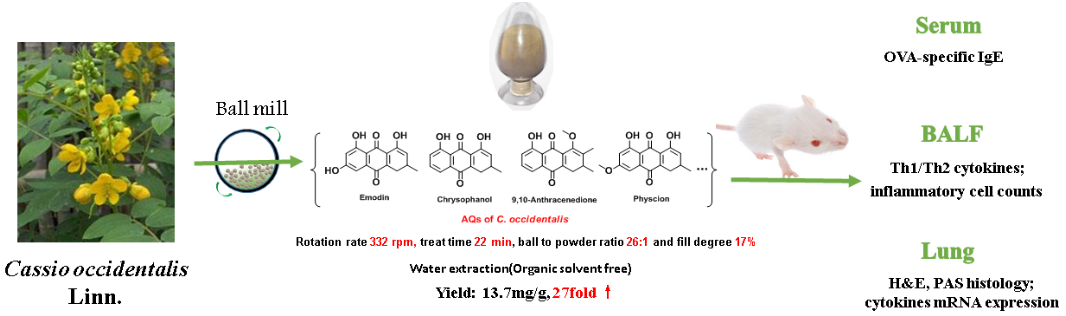

*Cassia occidentalis Linn* is a herb medical containing anthraquinones (AQs) as the principle active constituents. In folk medicine, it has a variety of uses including treatment of whooping cough (“pertussis”) and inflammatory diseases. But organic solvent as chloroform which is harmful to human and environment are still used to extract AQs. So green and effective way to extract AQs is urgently needed and more investigations are also imperatively required to validate the effects of the AQs found within *Cassia occidentalis Linn* on airways inflammation in asthma.

Mechanochemically assisted organic free extraction of AQs from *Cassia occidentalis Linn* was performed and the conditions of mechanochemical treatment were further optimized with response surface methodology. For operational convenience, the optimal mechanochemical treatment parameters were set as: rotation rate 332 rpm, treat time 22 min, ball to powder ratio 26:1 and fill degree 17%, respectively. The resultant AQs extraction yield was of 13.7 mg/g. which exceeds the traditional one (0.495 mg/g) in 27 time.

Meanwhile, to explore the anti-inflammatory potential of AQs extracted from *Cassia occidentalis Linn* using an in vivo model of ovalbumin (OVA)-induced asthma. After experiments, we found that treatment with AQs and rhein decreased inflammatory cell counts and production of Th2 cytokines IL-4, IL-5 and IL-13 in BALF, and OVA-specific IgE in serum. In contrast, Th1 cytokine IFN-γ production in BALF was promoted. AQs also decreased mRNA expression of Th1/Th2 cytokine in lung tissue. Histological studies demonstrated that AQs substantially inhibited OVA-induced cellular infiltration, mucus hypersecretion and goblet cell hyperplasia in the lung.

These findings demonstrated that mechanochemical treatments could significantly increase extraction rate of AQs in *Cassia occidentalis Linn*. The AQs showed great inhibitory effects on OVA-induced allergic asthma in mice. The results suggest a way to extract AQs from *Cassia occidentalis Linn* and provide a promising ethnopharmacological use for it in patients with asthma.

# PREPARATION, CHARACTERIZATION, IN VITRO AND IN VIVO STUDIES OF OLMESARTAN MEDOXOMIL IN A TERNARY SOLID DISPERSION WITH N-METHYL-D-GLUCAMINE AND HYDROXYPROPYL-Β-CYCLODEXTRIN

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Olmesartan medoxomil (OM) has been used in treatment of hypertension disease, as a prodrug of olmesartan. However, its clinical application is limited by the low oral bioavailability (~28%). Preparation of ternary solid dispersion of OM improves its oral bioavailability. The ternary solid dispersion of OM was environment-friendly prepared with N-methyl-D-glucamine and Hydroxypropyl-β-cyclodextrin using VM-1 roll mill. Its physical characteristics were measured by differential scanning calorimerey, powder X-ray diffraction and Fourier transform infrared spectroscopy. In vitro and in vivo properties of OM in ternary solid dispersion were investigated, involving the dissolving behavior, solubility, dissolution profiles and oral bioavailability. Experimental data have revealed that the amorphous solid dispersion was synthesized without any by-products.

The synthesized solid dispersion promoted the breakage of ester to olmesartan in water solution. It also showed enhanced solubility and dissolution rate in vitro, as well as an improved oral bioavailability in vivo. The synthesized OM ternary solid dispersion promises better alternative for formation of pure medical substance with the improved oral bioavailability.

# PREPARATION OF CURCUMIN SOLID DISPERSIONS WITH ENHANCED BIOAVAILABILITY AND CYTOTOXIC ACTIVITY BY MECHANOCHEMISTRY

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Pharmaceutical solid dispersions (SDs) of curcumin (Cur) with disodium glycyrrhizin ($Na_2GA$) and complexation agent - polysaccharide arabinogalactan (AG) from wood of *Larix Sibirica* were prepared by ball milling. The physical properties of the obtained SDs in solid state were characterized by scanning electron microscope, differential scanning calorimetry and X-ray diffraction studies. The behavior of SDs after dissolution in water was characterized by reverse phase HPLC, $^1$H-NMR spectroscopy, UV-Visible spectroscopy and gel permeation chromatography (GPC). Curcumin loaded micelles were self-formed by $Na_2GA$ when SD dissolved in water. Significant improvement of Cur solubility by formation of micelles and intermolecular complexes of guest-host type with arabinogalactan macromolecules was demonstrated. In vitro cytotoxic tests demonstrated that Cur SDs induced higher cytotoxicity against glioblastoma U-87 MG cells than free Cur. Besides, an improvement of membrane permeability of Cur SDs was confirmed by parallel artificial membrane permeability assay. Further pharmacokinetic study of SDs formulation in rat showed a significant 8~19-fold increase of bioavailability as comparing to free curcumin. Thus, Cur SDs provide a more potent and efficacious formulation for Cur oral delivery.

# OBTAINING OF POWDERS OF INFRARED DRYING VEGETABLE RAW MATERIALS FOR THE OPTIMIZATION OF BAKERY PRODUCTS

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The purpose of this work is to investigate the possibility of processing plant raw materials and obtain infrared (IR) dried fine powders for the enrichment of food products with biologically active substances. The raw material was IR dried with subsequent mechanical grinding. The fine powders of carrots, beets and cranberries were obtained. After mechanical and mechanochemical activation of samples with various additives, the maximum amount of water-soluble substances was determined. Mechanical activation of the samples was carrying out in the planetary mill of activator type – APF. It is established that the percentage of water soluble substance in powders increases after their mechanochemical activation. The largest yield was achieved in the powder of IR dried carrots after adding 5% $NaHCO_3$ (before treatment ~ 37%, after treatment ~ 62%).It was found that carrot powder contains a large amount of β-carotene (0.67 ± 0.07 mg), and beet and cranberry have a high antioxidant activity (1.2 ± 0.2 and 8.9 ± 0.9 μg quercetin/g product, respectively), which allows them to be used as ingredients in the development of functional food products. We developed a line of the baked goods prepared on the basis of dry demineralized whey "WimmBillDann" with addition of egg shell powder in combination with herbal powders. The optimal ratio of the main components was determined using the method of mathematical modeling. Egg shells after treatment and calcination are crushing in the disintegrator Desi-11. The weighted average particle size of 25 μm was determining by laser beam diffraction on the device Microsizer 201. According to the results of the research, it was found that the calcium content in the crushed shell was 54%, protein – 15%. Finished products were studying in terms of quality. It was established that the addition of egg shell powder will enrich bakery products with calcium, and the addition of vegetable powders increase the digestibility of calcium, enrich products with β-carotene, antioxidants and improve consumer characteristics of bakery products.

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# THE USE OF ENCAPSULATION TECHNOLOGY FOR IMPROVEMENT OF FUNCTIONAL PROPERTIES OF CURD DESSERTS

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The aim of the work is to use various methods of encapsulation to improve organoleptic properties of functional products, including curd desserts. Rowan and its products contain a complex of biologically active substances, including antioxidants. After preliminary grinding dried fruits in a disintegrator, fine powder with a pronounced smell of Rowan and bitter taste was obtained. To compensate undesirable organoleptic characteristics, the encapsulation technology consisting of joint spray and freeze-drying was used. Konzhak and guar gum were chosen as the encapsulating matrix, respectively. The ratio of complexes was established as 1:1 and 1:2. Since spray drying gives a small powder yield, powder after freeze-drying was used to optimize desserts. Descriptive profile method of tasting analysis showed that encapsulated powder has a creamy color, delicate taste, lack of bitterness. Antioxidant activity (μg quercetin/g of product) of Rowan at baseline (4.2±0.5), IR drying powder (5.6±0.3) and encapsulated powder (2.4±0.2), flavonoid content in IR drying powder-2.2 mg/g, in encapsulated powder-1.45 mg/g and β - carotene in IR powder (15.2±0.2) and encapsulated (8.1±0.1) were determined. Taking into account the dilution of Rowan powder by polysaccharide (1:1) the total content of antioxidants, flavonoids and β-carotene in the resulting powder is not reduced. Technologies and formulations of curd desserts were developed with IR powder (2%, 7%) and encapsulated powder (14%). The concentration of powders in the formulation was determined by the method of mathematical modeling. The mass fraction of the quality criteria for each sub-component was taken from the standard documentation. The finished samples have high organoleptic characteristics. Physico-chemical study has confirmed the functional properties of desserts that satisfy more than 15% of the daily requirement for antioxidants and β-carotene. Experimental investigations in cooperation with ISSCM SB RAS have proved that the use of encapsulation technology does not reduce the nutritional value, antioxidant activity of powders and has a positive effect on consumer properties of the product.

This study was supported by the Russian Science Foundation (grant no. 16-13-10200).

# MECHANOCOMPOSITES OF PIROXICAM WITH CHITOSAN OF DIFFERENT MOLECULAR MASS

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Piroxicam is a non-steroidal anti-inflammatory drug, which is poorly soluble in water. In this work, to improve the rate of dissolution and the solubility of the drug, the mechanocomposites of piroxicam with biopolymer chitosan were obtained.

High molecular weight (HMW) chitosan ($M_w$ = 460 kDa) and water-soluble low molecular weight (LMW) chitosan ($M_w$ = 39 kDa) were used as the carriers. Mechanical treatment of the mixtures of piroxicam with chitosan (1:3 and 1:10, w/w) was carried out in two ball-mills, namely, a SPEX 8000 mixer mill (CertiPrep Inc, USA) and a planetary AGO-2 mill (ISSCM, Russia). Both mills proved to be effective for producing piroxicam-chitosan composites. It was shown that HMW chitosan and LMW chitosan were useful for improving the dissolution behavior of piroxicam. Interestingly, in the case of HMV chitosan, the rate of drug release and its solubility were higher than those for the LMW polymer. A possible cause is cracking of the polymer chains and a decrease in its molecular weight during ball-milling. On the other hand, mechanical activation leads to the formation of molecular complexes of piroxicam with chitosan due to hydrogen bonding between the components. The most soluble samples were the mixtures of separately milled components due to complexation in solution. However, the release of piroxicam from the mechanocomposite occurs at a higher rate because of the distribution of chitosan in the polymer and the formation of molecular complexes. The use of LMW chitosan as a carrier leads to an increase in the solubility of piroxicam to a lower degree, which can be related with the different structure of intermolecular piroxicam-chitosan complexes. The studies of the pharmacological activity showed that piroxicam - chitosan mechanocomposites displayed more potent analgesic activity than initial piroxicam.

# MECHANOCHEMICAL SYNTHESIS OF COCRYSTALS OF BETULIN

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Betulin is a pentacyclic triterpene alcohol which can be obtained from birch bark. Betulin has a wide spectrum of biological and pharmacological activities but it exhibits very poor water solubility, which clearly reduces its bioavailability. The preparation of co-crystals, i.e. multi-component crystals of an active pharmaceutical ingredient (API) with water-soluble, non-toxic partner molecules is often used in pharmacy as a strategy for altering the physico-chemical/solubility properties of the API. In this paper, the cocrystals of betulin were prepared for the first time using adipic acid as a coformer. It was shown that due to strong propensity of betulin to form solvates, solvent crystallization technique gave mainly the solvates of betulin. To prepare betulin cocrystals, liquid-assisted grinding method was used with the solvents of different polarity. The mixtures of betulin with adipic acid were ball-milled in a SPEX 8000 mixer mill (CertiPrep Inc., USA) in a 60 mL steel jar with the balls of the same material and 6 mm in diameter. Previously, the mixtures were milled in dryness for 5 min, then 1 mL of solvent was added, and the paste was subsequently milled for 10 min. The formation of cocrystals was confirmed by powder X-ray diffraction and IR spectroscopy. The results obtained by thermal analysis methods and powder X-ray diffraction suggested that cocrystal hydrate containing the betulin – acid – water components in 1:1:1 ratio was formed when liquids miscible with water were used for liquid-assisted grinding. The stability of the cocrystals obtained was evaluated by thermal analysis and hot-stage microscopy methods. Under controlled temperature and rather high relative humidity, the cocrystal hydrate was stable. Nevertheless, it has low thermal stability due to the facile loss of the crystal lattice water molecules, followed by phase transformation and cocrystal dissociation. The solubility study showed that the solubility of the betulin cocrystal hydrate was significantly improved in comparison with initial betulin and its composites with polymers.

# EFFECT OF BALL-MILLING ON PREPARATION OF COMPOSITES OF BETULIN AND BETULIN DIACETATE WITH POLYETHYLENE GLYCOL

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Polyethylene glycol (PEG) is a promising solubilizing agent and is often used for preparation of composites of poorly water-soluble drugs using, among others, mechanochemical methods. Due to the low melting point of PEG, the interaction of the components under ball-milling can be facilitated by melting of solids at the contacts of particles under collisions or ball impacts. Previously [1], we reported on preparation of the composites of betulin and betulin diacetate (BDA) with PEG by ball-milling. They exhibited higher solubility of betulin and improvement of its biological activity. At the same time, the composites of BDA with PEG did not reveal high solubility of the drug compared to the initial substance. The purpose of this work was to study the mechanism of formation of the composites of betulin and betulin diacetate with PEG under ball-milling. The mixtures of betulin or BDA with PEG (1:3 or 1:9, w/w) were ball-milled in a SPEX 8000 mixer mill (CertiPrep Corp., USA) for 15 or 30 min. The steel jar (60 mL) and steel balls with diameter 6 mm were used. In case of PEG – betulin mixtures, there was almost complete amorphization of betulin under ball-milling. On the contrary, there were no significant changes in the intensity of the lines in the PXRD patterns for ball-milled PEG-BDA mixtures. Dissolution of BDA in PEG melts formed at the contacts of particles under collisions with milling bodies leading to recrystallization of the drug was suggested. Hot stage optical microscopy study confirmed the possibility of dissolving of BDA crystals in PEG melt. Dissolution of betulin in PEG proceeded at higher temperatures than dissolution of BDA resulting in disordering of its crystal structure under ball-milling.

[1] Mikhailenko M.A., Shakhtshneider T.P., et al. Chem. Nat. Comp. 47 (2011) 229-233.

# EFFECT OF MECHANICAL TREATMENT ON MICROWAVE-ASSISTED SYNTHESIS OF SUPRAMOLECULAR COMPLEXES OF BETULIN DIACETATE WITH ARABINOGALACTAN

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Betulin diacetate (BDA) exhibits versatile biological activities but the poor solubility in water limits its application. Previously [1], we reported on the mechanochemical preparation of the composites of BDA with water-soluble polysaccharide arabinogalactan (AG) possessing a higher solubility due to complex formation. In this work, a water-soluble BDA - AG complex was synthesized in an aqueous suspension of the components upon microwave heating (Discover-S-Class, CEM, USA). Microwave heating allows significant reducing the time required for the complex formation. After evaporation of the suspension filtrates, a thin flexible film was obtained which was characterized by complete dissolution in water and increased biological activity. It could be expected that mechanical activation will cause an increase in the reactivity of the reactive mixture in the microwave-assisted synthesis. Ball-milling of the 1 : 9 (w/w) BDA-AG mixture was carried out in a SPEX 8000 mixer mill (CertiPrep Inc., USA) in a stainless steel vial (60 mL) with steel balls (6 mm in diameter, total 30 g) for 15 min. Then the suspension of the ball-milled mixture was subjected to microwave heating. Nevertheless, proceeding ball-milling of BDA-AG mixtures had an adverse effect on the formation of the BDA-AG complex, resulting in a decrease in the product yield. It is likely that under milling, BDA was dispersed, and it covered the surface of AG particles preventing their subsequent dissolution. The presence of AG in the precipitate after the filtration of the microwave-irradiated suspension confirmed this hypothesis.

[1] Shakhtshneider T.P., Kuznetsova S.A., et al. Chem. Nat. Comp. 49 (2013) 470-474.

# CHANGE IN THE DEGREE OF CRYSTALLINITY OF α-CELLULOSE AND PLANT RAW MATERIAL UNDER MECHANICAL TREATMENT

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The determination of the degree of crystallinity is especially important in the study of the supramolecular structure of natural cellulose since the ratio between the content of crystalline and amorphous cellulose determines the reactivity of lignocellulosic substrates in subsequent actions, for example, in hydrolysis [1].

The goal of the present work was to study the disordering of the crystal structure of individual α-cellulose and cellulose composing the plant raw material using the shear and shock-shear mechanical actions.

By Segal’s, Rietveld’s, and Lorentzian deconvolution, it is shown that the degree of amorphization of α-cellulose and native cellulose composing the plant raw material is significantly dependent on the time and intensity of the mechanical action. The amorphization of pure α-cellulose and wheat straw occurs more efficiently in the AGO-2 planetary ball mill with shock-shear type of action. The change in the degree of crystallinity of the samples agrees with the diffraction pattern of the diffuse halo formation.

The comparison of the crystallinity values during activation in the RM-20 semi-industrial mill with shear type of action indicates a less intense effect on the α-cellulose and cellulose of the plant material, due to the shorter duration of the mechanical action on the sample [2]. Particle agglomeration is observed for α-cellulose, which makes it necessary to increase the power intensity of the mechanical activation.

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# EFFECT OF DISENTEGRATOR TREATMENT ON DISPERSITY AND PHYSICAL-CHEMICAL CHARACTERISICS OF HYDROLYSIS LIGNIN

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Ethanol obtained by hydrolysis of lignocellulosic raw material has the potential to replace fossil gasoline as a motor fuel on large scale. To be competitive with gasoline the production costs must be reduced by benefit utilization of solid non hydrolyzed residue (further hydrolysis lignin) the yield of which consists about 40% of the feedstock. Lignin constituent is the major component of this residue. The condensation of lignin in processing conditions leads to the formation of stiff cross-linked three dimensional structures, making residue insoluble in conventional organic solvents, nevertheless the presence of significant amount of oxygen containing functional groups in its, able to covalent and Van der Waals bonding. In this work mechano-chemical activation of hydrolysis lignin matrix using laboratory scale disintegrator D -7119 (Tallinn, Estonia) was applied as pretreatment for further processing of commercial acid hydrolysis lignin aimed at high value product obtaining. It was shown, that dispersity, external and total specific surface area of hydrolysis lignin were increased significantly. Lignin treated in disintegrator has significantly more advanced pore surface at the similar dispersity than lignin crushed in ball mill. Besides that, the increasing of OH groups content in lignin and declining of its glass transition temperatures with increasing of rotors rotation rates was established. It can be explained by partial destruction of inter- and intra- molecular bonds in lignin. The incorporation of hydrolysis lignin treated in disintegrator into the composition on the basis of flour containing gum SKF-40 and SKEPT-40 revealed the increasing of tensile strength of elastomers by 30-40% higher than that obtained at the incorporation of lignin crushed in ball mill. The Banbury type internal mixer allowed to promote and realize synthesis of organo-inorgano hybrid material by coupling of hydrolysis lignin with Si- containing compounds able to react with OH groups of lignin and additionally to interlock with matrix structure units. The hybrid materials contained of 10-20% chemically bonded -O-Si-O- revealed the enhanced sorption activity due to formation of micropores absent in parent matrix. It was shown that pre-treatment of hydrolysis lignin in disintegrator leaded to more effective modification of hydrolysis lignin matrix by Si – containing compounds.

# MECHANOCHEMICAL SEA BUCKTHORN PRODUCTS AS FODDER ADDITIVES FOR PIGS

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Adaptation problems of agricultural animals to farming technologies and natural environments are actual for husbandry and veterinary. Multifunctional activity of nervous and endocrine systems is in the base of physiological mechanisms of adaptation. The state of nervous and hormonal regulation depends upon the concentration of some biologically active substances animal organisms. Serotonin plays a regulative role in the excitation and inhibition physiological processes. The sea buckthorn is very perspective source of serotonin, containing this substance in a various part of a plant, sometimes more than 1 mass %.

The modern tendency of last decades is an application of mechanochemical method to production of biologically active preparations from plants (leaves, bark, branches, waste of berries extraction, relatively). Technology of serotonin preparation production consist in mechanical treatment of mixture of plant powder and solid reagent in special mechanochemical mill – activator under condition allowing chemical reaction of serotonin with formation of water soluble form and stability of used substances. Synthetic serotonin is not competitive with natural one from economical point of view. Powders produced in solid state mechanochemical technology were used in experiment as an additive for the foddering of sucking-pigs 5 – 60 days old. Experimental data are in the table:

| | Group | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| Content of fodder | General daily diet (GDD) Control | GDD + 1% mixture № 1 | GDD + 1% mixture № 2 | GDD + 1% mixture № 3 | GDD + 1% mixture № 4 |
| Living mass, kg | 13,13 | 16,06 | 18,39 | 17,12 | 15,47 |
| Daily average increase, g | 217 | 284 | 343 | 313 | 270 |
| Feed spendings for increase 1 kg of leaving mass, feeder unites | 1,92 | 2,09 | 2,14 | 2,28 | 1,90 |

The use of serotonin containing products can increase daily increase of animals up to 58 %.

# FRACTIONATION OF PLANT MATERIALS (ON THE EXAMPLE OF PEA SEEDS) AND STUDY OF PHYSICAL AND CHEMICAL PROPERTIES OF THE SELECTED PROTEIN AND CARBOHYDRATE FRACTIONS

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At present, there is an acute need of the population of Russia in food products enriched by proteins, in natural form and with a modified structure and increased bioavailability. To create a mechanoenzymatic technology for the hydrolysis of protein plant material, it is required to obtain fundamental knowledge about mechanochemical transformations in separate components of plant raw materials (proteins, carbohydrates, etc.) and their complexes [1].

The purpose of this research was to divide plant materials into protein and carbohydrate fractions and to study the properties of the fractions obtained by modern methods of qualitative and quantitative analysis.

The preparation of fractions with different content of proteins and carbohydrate was carried out according to the procedure based on triple extraction with sodium hydroxide, published in [2]. The protein-carbohydrate fractions obtained by precipitation from the extracts were washed with cooled ethanol and prepared for freeze-drying. Quantitative analysis of the protein was carried out according to the method of Lowry. Qualitative analysis of the protein molecules in the obtained fractions was carried out by electrophoresis in a polyacrylamide gel.

Thus, four fractions containing in different ratios of macromolecule of protein and natural carbohydrate were obtained from protein-containing raw materials and characterized. The results of the work will be used to obtain fundamental knowledge of the mechanochemical transformations required for setting mechanoenzymatic technology for the production of components of functional foods and feeds.

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# THE CONCENTRATION OF SOLUBLE BIOLOGICALLY ACTIVE SUBSTANCES IN POWDER MATERIALS OBTAINED FROM WOODY MUSHROOMS BY THE MECHANOCHEMICAL METHOD

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Powder materials obtained from mushrooms differ from products of vegetable and animal origins. Mushrooms occupy an intermediate position between plants and animals based on their structure and metabolism. More than a hundred of them have long been used in traditional medicine of China, Korea, Japan and other countries of South-East Asia. This class includes mushrooms that are popular in folk medicine: Reishi - tinder conk mushroom (*Fomes fomentarius*), shiitake (*Lentinus edodes*), which has surpassed the traditional champignons and oyster mushrooms in production volumes, and chaga.

The main active ingredient that provides the biological activity of pharmacological drugs is a dark polyphenol carbon complex containing strong antioxidants, melanins. The concentration of melanins is particularly high in tinder mushrooms.

The use of solid-phase mechanochemical methods opens up prospects for the production of powder preparations with increased yield and dissolution rate in aqueous media.

Powders of woody mushrooms are slightly acidic, and pH of solution in the extraction is 4.3-5.6. The following mixtures of mushroom powder and solid reagent (5 w.%) with increasing alkalinity were used for mechanochemical treatment: $NaHCO_3$, $Na_2CO_3$, NaOH. The high reactivity of composites is predetermined by a larger contact area and the reduction of diffusion difficulties.

The concentration of water-soluble substances was determined. For chaga we can see that an increase in the concentration of water-soluble substances from 26 to 33% enhances melanin concentration from 21 to 30%. The concentration of water-soluble substances can be used for rapid analysis of the quality of mushroom powders obtained by mechanochemical method.

Thus, the highest concentration of soluble substances of polyphenolic nature including melanin in powders obtained from woody mushrooms is achieved by solid-phase mechanochemical treatment using solid alkalis.

# OBTAINING OF NANOFILMS BASED ON Ag-CHITOSAN/Na-CARBOXYMETHYL CELLULOSE ON THE SURFACE OF TITANIUM IMPLANTS

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Titanium (Ti) and its alloys are widely used in orthopedic implants due to their excellent biocompatibility and mechanical properties. However, titanium-based implant materials have specific complications associated with poor cell adhesion and susceptibility of implants to bacterial infections. In this regard, an actual problem in practical medicine is the application of antibacterial and anti-inflammatory agents to the surface of implanting medical and biological products. Various physicochemical methods are used for this. The most promising method from the point of view of ecology, simplicity and cheapness is the multilayer assembly method, based on the acid-base electrostatic interaction of polyelectrolytes.

The results of this study are aimed at establishing optimal conditions for obtaining antibacterial coatings on the surface of titanium with improved biocompatible properties. As an antibacterial agent, silver particles were used. Chitosan and Na-carboxymethyl cellulose were used as biocompatible polyelectrolytes for multilayers. Chitosan, which has natural antibacterial activity, can also serve as a stabilizing ligand for silver ions, since the amino groups of chitosan can chelate silver ions and nanosized particles through coordination interaction. Preliminary, optimal conditions for activating the surface of implants with solutions of sulfuric acid in the presence of hydrogen peroxide (piranha) were established. The thickness of the multilayers increases linearly with increasing bilayers on the surface of the plates. The roughness depends on the nature of the polyelectrolytes and the pH of the medium. The results of scanning microscopy unambiguously showed the presence of silver particles on the surface of nanofilms, and elemental analysis confirmed these data. The obtained experimental data allowed to develop the conditions for obtaining of multilayers with silver particles with good antibacterial properties. Preliminary tests showed good antibacterial activity of the multilayers in relation to the museum strain E. coli ATCC25922 and the wild P.Aeruginosa strain.

# SOLID-PHASE REFINERY PRODUCTS OF MECHANOCHEMICAL TREATMENT OF PLANT RAW MATERIALS

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Plant raw materials have a high industrial potential. The study and development of methods for mechanochemical activation of plant raw materials is an urgent task nowadays. It is also of interest to study solid-phase reactions that occur during the mechanical treatment.

It is assumed that tissue with a high content of lignin will have greater hardness during mechanochemical treatment. After the destruction, they will retain the original porous structure.  Particles with a low content of lignin will have a higher density after destruction due to the collapse of cell pores. Thus, particles with different lignin contents will differ in density. This makes possible their aerodynamic separation. Consequently, it is possible to isolate fractions with an increased content of the target biologically active substances.

The aim of our work is to study the possibility of solid-phase aerodynamic enrichment of plant raw materials throughout its mechanochemical treatment and subsequent separation into fractions. The experiments were conducted with several classes of compounds: polyphenolic compounds - green tea catechins; naphthodiantronic compounds of St. John's wort; serotonin, contained in the sea buckthorn bark as an alkaline compound; humic acids of brown coal. The relevance of the study of phenolic compounds of plant raw materials is associated with their antioxidant activity.

Plant raw materials were mechanochemically processed in a TM-3 activator mill (Novits, Novosibirsk). The separation of fractions was carried out on the classifier InoxGrade (Inox, Novosibirsk). The frequency was 0 - 5920 rpm. The content of the target substances was analyzed by HPLC.

The content of serotonin was 3 times higher in the fractions obtained at high rotor speeds of the separator-rotor than in the raw material. In all cases, the extraction was exhaustive. The yield of serotonin does not depend on the particle size.

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# THE USE OF MECHANOCOMPOSITES OF GREEN TEA AS ANTIOXIDANT ADDITIVES FOR THE FORMULATION OF FUNCTIONAL FOODS

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The development of functional food products is an innovative direction of science that involves the scientist in the field of chemistry, biochemistry, as well as dietetics and medical prevention medicine. One of the most popular group on functional products is antioxidants.

The new formulations were developed at the Department of technology and organization of food production of Novosibirsk State Technical University. This work deals with formulations of blended juices [1]. Available raw materials, mainly of local origin, were used for juice preparation: apples, sea buckthorn, pumpkin, carrots, ginger and lemon.

To enhance the functional properties of new generation of products, additives with a high content of antioxidants were used. The functional additives were produced by mechanochemical treatment of green tea leaf. It was shown previously that mechanochemical treatment of green tea with ascorbic acid increase antioxidant activity of product and storage time [2]. The main sources of antioxidants are vegetable raw materials, including green tea leaf. Together with the Institute of Solid State Chemistry and Mechanochemistry SB RAS, the additive with an active complex of the antioxidants based on green tea has been developed. The high-quality raw materials (green tea), containing catechins which possess pronounced antioxidant properties, was used for its production. The optimal concentration of the tea additive was determined by experimental studies.

Ready samples of juice have been studied by organoleptic, physical and chemical and microbiological qualitative methods.It is established that new products possess high indicators of anti-oxidant activity, and also are a source of minerals (K; Fe) and vitamin C.

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# MECHANOENZYMATIC OBTAINING IN SOLID PHASE OF PROTEIN HYDROLYZATE FOR THE DEVELOPMENT OF NEW PRODUCTS FOR SPECIALIZED PURPOSES

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Experts estimate that 2 billion people suffer from protein deficiency, which leads to serious health risks. The search for new and alternative sources of protein is a topical topic of the world level.

Experts of the program "The Protein Challenge 2040" are considering the issue: «How can we meet the protein needs of 9 billion people in a way that is affordable, healthy and good for the environment». The Protein Challenge 2040 is a ground-breaking global coalition that brings together the animal, plant and novel protein industries, as well as global environmental and health organizations.

Enzymatic modification of food proteins by controlled hydrolysis decreases the chain length of polypeptides and brings about changes in functional properties. Specific properties of the hydrolysates are dependent upon the degree of hydrolysis, physical and chemical character of the protein substrate and reaction conditions. There is an optimum degree of hydrolysis beyond which any improvement gained in functional behaviour can be lost.

Within the framework of concept "The Protein Challenge 2040", at the Department of Technology and Organization of Food Production, in cooperation with the Institute of Solid State Chemistry and Mechanochemistry of the SB RAS, special purpose products obtained by mechanoenzymatic hydrolysis have been developed.

As a result of the conducted studies, by the determination of soluble amino acids, the effectiveness of the application of mechanoenzymatic hydrolysis of plant raw materials was substantiated. Developed products for specialized purposes are sources of protein and minerals.

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# INVESTIGATION OF THE UV RADIATION INFLUENCE ON OPERATING CHARACTERISTICS OF POLYURETHANE

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The influence of ultraviolet (UV) radiation on the operating characteristics of unmodified polyurethane (PU) and modified with silicon carbide nanoparticles ($d_{av.}$ = 50 nm) has been studied. SKU PFL-100 was used as a prepolymer. The characteristics of initial polyurethane are presented in Table 1.

Table 1. Operating characteristics of unmodified PU.

| Density, g/cm$^3$ | Hardness, Shore A | Breaking strength, MPa | Relative elongation, % |
|---|---|---|---|
| 1.09±0.02 | 94±1 | 28.1±1.2 | 625.1±16.3 |

* The cross-sectional area of working zone - 25 mm$^2$, its length - 35 mm.

The PU samples were placed into the box under UV radiator, the radiation intensity of which was of the order of 100 W/m$^2$, and the duration of exposure was 20 hours, the sample temperature did not exceed 40°C.

It was revealed that as a result of UV impact, the strength of samples on the basis of modified PU decreases by almost 2% (silicon carbide content 0.05%), whereas of that based on unmodified PU - by 18% (Fig. 1).

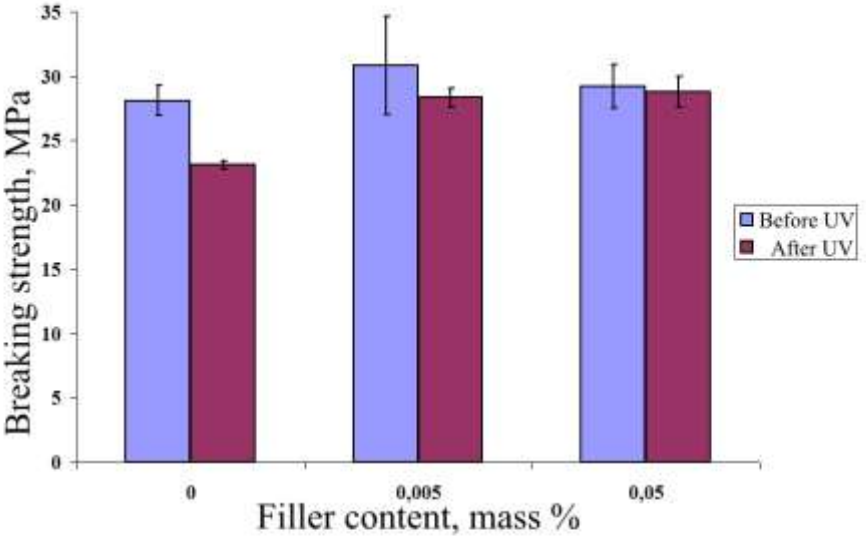

Fig. 1. UV radiation impact on polyurethane.

# INFLUENCE OF HIGH TEMPERATURES ON OPERATING CHARACTERISTICS OF POLYURETHANE

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The influence of heat treatment on the operating characteristics of polyurethane (PU) has been studied. SKU PFL-100 was used as a prepolymer. The characteristics of initial polyurethane are presented in Table 1.

Table 1. Operating characteristics of initial PU.

| Density, g/cm$^3$ | Hardness, Shore A | Breaking strength, MPa | Relative elongation, % |
|---|---|---|---|
| 1.09±0.02 | 94±1 | 28.1±1.2 | 625.1±16.3 |

* The cross-sectional area of working zone – 25 mm$^2$, its length – 35 mm.

It has been found that heat treatment of PU samples during 5 - 15 hours at the temperature of 120°C leads to the increase in strength up to 24% relative to the initial one. The further increase of the warm-up time also leads to the increase of their strength, but even at 35 hours of heat treatment the hardening is much lower, only 19% relative to the initial PU. The relative elongation of the PU samples does not practically change with the time (up to 35 h) of heat treatment (Figure 1).

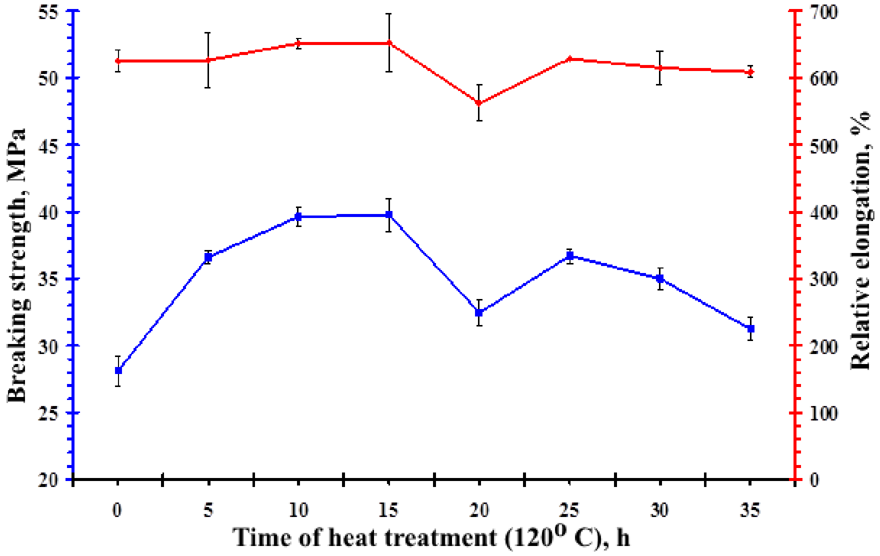

Fig. 1. The changes in the operating characteristics of PU depending on the time of heat treatment.

# CHANGE IN THE COLLOIDAL PROPERTIES OF HUMIC SUBSTANCES DURING MECHANOCHEMICAL ACTIVATION

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Surface active properties of humic acids (Has) are determined by structural features of macromolecules and conditions for the formation of associates and micelles in solution. The critical concentration of micelle formed in alkaline (pH = 11.5) or neutral (pH = 7) media for HAs from peat and coal is 0.7 ÷ 1 g/L. Mechanochemical activation of coals helps to reduce the CMC values to 0.5 g/L for extracted HA samples. This fact is explained by the increase in the content of functional groups in the molecular structure of carbon HAs. Mechanoactivated carbon samples of MOCHA and MBCHA are also characterized by a decrease in the length of aliphatic chains with functional groups at the ends and a decrease in dissociation constant pK $C_n$–COOH values and, correspondingly, an increase in the acid properties of these groups.

Micelles are formed in acidified solutions at pH = 4 and the HA concentration 0.05 g/L. The degree of dissociation of HA functional groups, ensuring aggregate stability of a system, decreases with pH decreasing. The micelles formed in acidified solutions of HAs are larger due to their higher surface active properties.

The size of colloidal particles of HAs has a dramatic impact on the stability of a disperse system. Aggregation in a colloidal system is a kinetic nonequilibrium process of particle growth. The size and structure of aggregates formed depend on the aggregation dynamics. The method of photon correlation spectroscopy demonstrated that for these samples the particle sizes reach 100-150 nm at pH = 11.5 and remain unchanged for 140 minutes. At pH = 8, the particles have a size of 150 nm at the initial time. The process of aggregation with time proceeds quite intensively and is satisfactorily described by a power law dependence, which characterizes the diffusion-limiting model of the aggregation of HA macromolecules. Particle sizes reach 2000 nm by the end of experiment. The processes of aggregation of the macromolecular HA at pH = 6 and pH = 4 differ only in the initial particle sizes of 500-550 nm and 750-800 nm, respectively. The average particle radius for these samples varies in time almost similarly with a significant increase in the aggregation rate.

# PHYSICOMECHANICAL CHARACTERISTICS OF COMPOSITE MATERIALS MODIFIED WITH MECHANICALLY ACTIVATED PARTICLES

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The results obtained indicate that mechanically activated modifiers exert an ordering effect on the polymer matrix, increasing the degree of crystallinity and forming quasicrystalline regions in the amorphous portion of the binder. It is established that in the periphery of a mechanically activated particle an ordered transition layer of sufficiently large dimensions is formed due to the action of weak electromagnetic fields generated by the particle due to the presence of its acquired or its own uncompensated charge. Mechanoactivated particles, being distributed statistically in the volume of the composite material, cause the formation of specific nodes of physical cross-linking of macromolecules, due to their adsorption on the active sites of the modifier. The prospects of using mixtures of mechanically activated particles in the modification of polymeric materials are shown. Synergic mixtures of mechanically activated particles have a large and prolonged effect on the physico-mechanical characteristics of the resulting mechanically activated composite materials. An increase in the melt viscosity of polyamide 6 was revealed upon the introduction of mechanically activated particles. Formulations of a composite thermoplastic material modified with mechanically activated particles that surpass analogues in terms of service characteristics of coatings deposited on both the original and modified surfaces are developed. The proposed composition can be used for the preparation of anti-wear and antifriction coatings for automobile aggregates, for example, for splined joints of cardan gears, guide pipe shock absorbers, springs of brake chambers. Thus, on the basis of physical representations, the formation of electrostatic (charge) mosaic areas in kaolinite, as well as in individual layer silicates, caused by substitution and displacement defects is shown on their surface.

# PROTON ELECTROLYTES IN THE SYSTEM OF HYDROPHOSPHATES OF RUBIDIUM, OBTAINED WITH THE HELP OF MECHANOCHEMICAL METHODS

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Solid acids $M_nH_m(AO_4)_p$ (M = alkali metal, A = P, S, Se) present an important class of electrolytes. These compounds exhibit anomaly high proton conductivity at intermediate temperature range (130-250°C) due to the superprotonic phase transition. Superprotonic conductors are of interest from both practical and fundamental points of view. Solid acids can be used for the design of perspective proton-exchange materials, particularly, as a component of the intermediate temperature fuel cells membranes. Despite this, hydrophosphates of rubidium are relatively underexplored.

The aim of our study was the investigation of the phase composition, thermal and transport properties of $(1\text{-}x)RbH_2PO_4\text{-}xRb_2HPO_4\bullet 2H_2O$ (x = 0–1) system. The samples of the composition $(1\text{-}x)RbH_2PO_4\text{-}xRb_2HPO_4\bullet 2H_2O$ (x = 0.1-0.67) were prepared by solid state synthesis. The phase composition was determined by X-ray powder diffraction. The sample x = 0.25 was found to be $Rb_5H_7(PO_4)_4$ phase. The crystal structure of $Rb_5H_7(PO_4)_4$ was characterized in [1]. The other samples had the form of two-phase mixtures: $RbH_2PO_4$ and $Rb_5H_7(PO_4)_4$ (x = 0.1, 0.2), or $Rb_2HPO_4\bullet yH_2O$ and $Rb_5H_7(PO_4)_4$ (x = 0.33, 0.5, 0.67).

It is firstly shown that $Rb_5H_7(PO_4)_4$ exhibits the superionic phase transition near 232°C. According to XRD the phase transition is reversible, and the reverse transition goes slowly. The interval of phase stability for $Rb_5H_7(PO_4)_4$ is narrow (about 10°) and neighbors with the partial dehydration. Partial dehydration in $RbH_2PO_4$ and $Rb_5H_7(PO_4)_4$ can be suppressed by enhanced humidity. Proton conductivity of the system was investigated by ac-impedance spectroscopy under high humidify conditions. The proton conductivity of $Rb_5H_7(PO_4)_4$ increases sharply reaching $10^{-2}$ S/cm due to the phase transition. High proton conductivity due to $RbH_2PO_4$ and $Rb_5H_7(PO_4)_4$ phases was also shown for x = 0.1-0.33 at 230-260°C. One can consider $Rb_5H_7(PO_4)_4$ as a new example of the superprotonic salt.

This research was carried out within the state assignment to ISSCM SB RAS (project 0301-2016-0020).

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# INFLUENCE OF MECHANOCHEMICAL TREATMENT ON TRANSPORT PROPERTIES OF COMPOSITE SOLID ELECTROLYTES BASED ON $[(C_4H_9)_4N]BF_4$

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It is known [1] that tetrabutylammonium salt $[(C_4H_9)_4]NBF_4$ has an ionic conductivity about $10^{-9}$-$10^{-6}$ S/cm in the temperature range of 60-160°C. Composite systems based on this salt may be promising solid electrolytes with conductivity occurring via anions. Surface modification will allow the introduction of active surface centers on the oxide surface, which will selectively interact with the anions of the sublattice in the intermediate area. The modification was achieved due to the surface deposition of barium fluoride from the alcoholic solution of barium nitrate and through mixing of the initial constituents at the temperature exposure. When the heterogeneous dopant is introduced, the temperature dependences of the conductivity demonstrate a conductivity increase by more than an order at T = 140 ° C. In this case, the activation energy is reduced in comparison with the pure salt. Aim of this work is the influence of preliminary mechanochemical treatment on transport properties and disordering of the organic ionic salt in $[(C_4H_9)_4]NBF_4$ – $Al_2O_3$ composites.

The work was supported by the grant from the Russian Foundation for Basic Research No. 16-33-60188.

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# OXYGEN EVOLUTION FROM NONSTOICHIOMETRIC BSCF PEROVSKITE PREPARED BY MECHANOCHEMICAL TECHNOLOGY

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Materials with mixed ionic-electronic conductivity (MIEC) are of interest for development of membrane reactors and electrochemical devices [1-3]. Their properties, such as efficiency of oxygen sorbents and SOFC electrodes, response time of sensors, oxygen permeability of ceramic membranes, etc. are determined by the oxygen exchange of MIEC oxides with the oxygen in gas phase.

Since MIEC oxides are grossly nonstoichiometric compounds, i.e. solid solutions with a wide range of homogeneity, their properties (structural, thermodynamic and transport) significantly depend on the oxygen content [4]. Thus, variation of temperature and/or oxygen partial pressure $pO_2$ during the experiment can result in a significant change of the stoichiometry. Hence, it can change the kinetic parameters of MIEC oxides during the data acquisition. Usually, this aspect is not taken into account during investigation of the oxygen exchange in grossly nonstoichiometric oxides. In our previous work we showed that this leads to incorrect conclusions about the oxygen exchange mechanism in MIEC oxides [5].

To consolidate this approach, well-known nonstoichiometric perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) was chosen as a model object. Thus, the aim of this study was to characterize the kinetics of the oxygen evolution from BSCF perovskite samples in the isostoichiometric mode and determine the effect of the oxide stoichiometry on the kinetic parameters of the process. Preparation of BSCF samples was performed by mechanochemical technology, which allows to reduce the synthesis time by 5-7 times.

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# $Na_4Fe_3(PO_4)_2P_2O_7$ AND $Na_{4-x}Li_xFe_3(PO_4)_2P_2O_7$ CATHODE MATERIALS PREPARED VIA MECHANOCHEMICAL WAY

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$Na_4M_3(PO_4)_2P_2O_7$ (M = Fe, Mn, Co, Ni) are new promising class of cathode materials for Na- and Li-ion batteries (LIBs) [1]. Sodium iron ortho-pyrophosphate $Na_4Fe_3(PO_4)_2P_2O_7$ (NFPP), first prepared by Kim *et al*. [2], has an orthorhombic structure with the $Pn2_1a$ space group, 3D intercalation channels for the Na diffusion and a theoretical capacity of 129 $mA \cdot h \cdot g^{-1}$. Its operating voltage (3.0 V vs. $Na/Na^+$, and 3.2 V vs. $Li/Li^+$) is the highest among Fe-based cathodes. The Li structural analogue of NFPP for LIBs cannot be prepared by direct synthesis. The aim of the present work was to develop the mechanochemically assisted solid-state synthesis of NFPP and to study the $Na^+/Li^+$ chemical and electrochemical exchange.

To prepare NFPP, the stoichiometric amounts of $Na_4P_2O_7$ (95%), $Fe_2C_2O_4 \cdot 2H_2O$ (99%), and $(NH_4)_2HPO_4$ (98%) were mechanically activated using a high-energy AGO-2 planetary mill and then heat treated in an Ar flow. The temperature of the completion of the synthesis and crystallization of the final product NFPP upon heating the activated mixtures was determined by TG/DTA combined with the mass-spectroscopic analysis. The mixed Na/Li compositions $Na_{4-x}Li_xFe_3(PO_4)_2P_2O_7$ were obtained by the $Na^+/Li^+$ chemical exchange with LiBr and electrochemical exchange upon cycling NFPP in a Li cell.

Composition, structure and morphology of the as-obtained Na/Li mixed materials were analyzed by XRD, SEM, EDX, FTIR, and Mössbauer spectroscopy. According to EDS analysis, the Na/Fe ratio changes from 1.3:1.0 for the initial NFPP to 0.8:1.0 for NFPP after cycling in a Li cell, which corresponds to the composition of $Na_{2.4}Li_{1.2}Fe_3(PO_4)_2P_2O_7$. Chemical exchange results in higher degree of exchange and the formation of the $Na_{1.9}Li_{2.1}Fe_3(PO_4)_2P_2O_7$ composition. Both compositions have the structure similar to the initial NFPP and show attractive electrochemical performance when operating in Li cells.

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# THE $LiFe_{0.5}Mn_{0.5}PO_4$ CATHODE MATERIALS: THE INFLUENCE OF SYNTHESIS METHOD ON ITS STRUCTURE, MORPHOLOGY AND ELECTROCHEMICAL PROPERTIES

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$LiFe_{0.5}Mn_{0.5}PO_4$ (LFMP), which combines good rate capability of $LiFePO_4$ and high potential of $LiMnPO_4$, is considered as the next generation of the olivine cathode materials because of low cost and environmental benign. The electrochemical response of the LFMP cathode materials is influenced by many interdependent factors, including local structure, transition metal mixing, the presence and the efficiency of the carbon coating, particles' morphology, etc., which can be tuned by varying the experimental conditions.

In the present study, we compared the structure, morphology, and electrochemical properties of the LFMP cathode materials prepared by the mechanochemically assisted solid-state synthesis (LFMP-SS) and the solvothermal synthesis (LFMP-ST). The samples were characterized in detail by XRD using Rietveld refinement, Mössbauer spectroscopy, SEM, TEM, galvanostatic cycling, and GITT.

All LFMP samples are single-phase materials crystallized in the orthorhombic structure (S.G. Pnma). According to SEM and TEM, low-temperature LFMP-ST sample displays nanoplatelets with the length about 100 and 200-300 nm along *a* and *c* direction, respectively, and with thickness 20-30 nm thickness in *b* direction, while carbon-coated LFMP-SS consists of irregular-shaped submicron particles.

According to galvanostatic cycling, carbon-free LFMP-ST shows only one sloping voltage plateau at 3.4 V, suggesting that only $Fe^{2+}/Fe^{3+}$ redox couple is electrochemically active [1]. The post-coating of LFMP-ST leads to occurrence of two peaks corresponding to the $Fe^{2+}/Fe^{3+}$ and $Mn^{2+}/Mn^{3+}$ redox couples that indicates the occurrence of the cation rearrangement in the structure, also observed for LFMP-SS. However, LFMP-SS shows the electrochemical performance due to formation of more efficient carbon matrix.

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# MECHANOCHEMICAL SYNTHESIS OF A NEW COMPOSITE $Na_3FePO_4CO_3$/C CATHODE MATERIAL FOR SODIUM-ION BATTERIES

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Because of low abundance of Li in the earth crust and its high cost, the Na-ion batteries (NIBs) are rapidly developed last years to replace the Li-ion batteries (LIBs). The operating mechanism of NIBs is similar to LIBs with the $Na^+$ ions shuttling between electrodes instead of the $Li^+$ ions. However, number of the Na electrodes is much lower because of higher ionic radius of the $Na^+$ ions. A special attention is given for the polyanion-type cathode materials. DFT calculations predicted a novel class of mixed polyanion compounds – sodium metal carbonophosphates - as promising cathode materials for NIBs [1]. Carbonophosphates are a rarely explored chemical class of materials, which was previously found only among minerals, such as sidorenkite and bonshtedtite [2]. Among them, $Na_3FePO_4CO_3$ (NFPC) is one of the most perspective materials. NFPC crystallizes in the monoclinic structure with a $P2_1/m$ space group and 2D diffusional channels.

Because of low thermal stability of NFPC, the formation of carbon composites NFPC/C is not applicable at high temperature. Therefore, new synthesis ways to get NFPC/C are required. In the present study, we developed a new approach to prepare high conductive NFPC/C composite via combined hydrothermal and mechanochemical methods.

The as-prepared material was studied by XRD, Mössbauer spectroscopy, FTIR, EIS, and galvanostatic cycling. Rietveld refined lattice parameters correlate with the literature data [3]. Analysis of the Mössbauer spectra indicates that about 50% of the iron ions in NFPC are in the $Fe^{3+}$ state, evidencing that the exact formula of the as-prepared material can be described as $Na_{2.48}FePO_4CO_3$. The electrochemical behavior of NFPC/C has been tested in the 2 - 4.4 V range at different cycling rates. The average operating voltage is 2.65 V and the specific discharge capacity is 91 mAh/g, which corresponds to 95% of the theoretical capacity.

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# STRUCTURE AND OXYGEN PERMEABILITY OF MO-CONTAINING BSCF PEROVSKITE

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Nonstoichiometric perovskite ceramic membranes with mixed oxygen-electron conductivity (MIEC) attract increasing attention because of the possibility to use them in air separation technologies, as materials for catalytic membrane rector for partial oxidation of hydrocarbons [1]. Moreover, these oxides are a good candidate for cathode materials for solid oxide fuel cells (SOFCs).

In this work, nonstoichiometric oxides with perovskite structure $Ba_{0.5}Sr_{0.5}Co_{0.8-x}Fe_{0.2}Mo_xO_{3-\delta}$ ($0<x<0.15$) were prepared by mechanochemical solid state reaction method from metal’s oxides and carbonates ($SrCO_3$, $Ba(NO_3)_2$, $Fe_2O_3$, $Co_3O_4$, $MoO_3$). The stirring of stoichiometric reagents mixture was carried out in a planetary ball mill AGO-2, thus to reduce the temperature of the synthesis. In the final step the samples were sintered in air at 1150$^o$C for 6 hours.

It was shown that the $Ba_{0.5}Sr_{0.5}Co_{0.8-x}Fe_{0.2}Mo_xO_{3-\delta}$ ($0<x<0.15$) samples possess specific microstructure consisting of double perovskite domains distributed in the cubic perovskite matrix that results in the suppression of undesirable «cubic–hexagonal» phase transition at $x\geq0.02$. Doped materials demonstrate enhanced conductivity, high oxygen exchange properties and chemical compatibility with $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ electrolyte that allows to consider them as promising cathode materials for intermediate temperature SOFC.

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# PECULIARITIES OF THE STRUCTURE OF COMPOSITE MATERIAL OBTAINED ON THE BASIS OF BN - (TiN, AlN) AFTER MECHANICAL ACTIVATION AND SINTERING UNDER PRESSURE

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The increased level of mechanical characteristics of composite materials (CM) based on cubic boron nitride (*c*BN) is largely determined by the dispersion of the material structure [1]. As a rule, micro and nanostructured powders of *c*BN, as well as highly dispersed powders of refractory nitrides TiN, AlN, etc., obtained by plasma chemical synthesis or SHS, are used to obtain such CM.

On the other hand, the formation of a highly disperse structure in composite ceramics is possible if to use mechanically activated reaction components mixture as the initial materials [2, 3]. Thus, the aim of the work is to study the structure of CM obtained from powder mixtures BN–AlN and BN–AlN–TiN after mechanical activation (MA) and sintering under high pressure. As the initial powders, hexagonal boron nitride hBN with the particle sizes within 100 μm, hexagonal aluminum nitride hAlN of plasma-chemical synthesis with the particle sizes in the range of 1-5 μm, as well as titanium nitride TiN with a particle sizes up to 10 μm were used. MA of *h*BN and *h*AlN powders, as well as powder mixtures of *h*BN–*h*AlN and *h*BN–*h*AlN–TiN were carried out in a vertical attritor with impeller rotation speed of 700 rpm.

MA of the mixture of the initial *h*BN and *h*AlN powders leads to an increase in their specific surface area and decreases particle size to 30-300 nm. With a duration of MA in the range of 15-30 min, amorphization of the initial hexagonal phase of AlN and partial formation of the cubic AlN with a lattice parameter a = 0.412 nm are observed. The particle size of the powders mixture *h*BN–*h*AlN–TiN after MA is in the range of 0.5-1 μm. Sintering under pressure of mixtures after MA leads to the formation of nanostructured ceramic materials, the phase composition of which depends on the technological parameters of sintering.

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# MECHANOCHEMICAL ACTIVATION AND MODIFICATION OF METAL POWDERS FOR ENERGETIC CONDENSED SYSTEMS

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The development of new energetic materials will be greatly emphasized, primarily because of the importance of their practical application in various industries. Such materials have been used in practice since the discovery of gunpowder, and modern termite mixtures, explosives and rocket fuels are indispensable in many industries.

This work presents the results of mechanochemical treatment (MCT) of metal powders (aluminum and magnesium) in a dynamic action mill using surface active additives to improve the dispersity of powders and modify the surface layer of particles. The mechanical treatment of metals with modifiers promotes a change in the structure and composition of the surface of metal particles, an increase in the proportion of the active metal, and the formation of an organic coating of dispersible particles. The effect of mechanochemical treatment of metal powders on the process of technological combustion of thermite mixtures is studied. The results of the research showed that use as fuel components of aluminum and magnesium after MCT in the presence of modifiers leads to improving of thermo-kinetic characteristics of combustion process. Method of MCT also makes it possible to obtain highly dispersed modified material in a large volume, which is efficient from a technological point of view.

# MECHANOCHEMICAL SYNTHESIS OF INERT COMPONENT FOR COMPOSITE SOLID ELECTROLYTES BASED ON $CsNO_2$

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Solid–state electrochemical devices are one of the outstanding achievements in the development of science and technology. To create them, solid electrolytes with high ionic conductivity are needed. The search for new solid electrolytes is an urgent task in chemistry. Composite solid electrolytes are a relatively new class of solid electrolytes characterized by high ionic conductivity ($10^{-3}$-$10^{-1}$ S/cm), mechanical and thermal stability over a wide range of temperatures. Such electrolytes consist of two components: an ionic salt of MX type and an inert oxide additive A. An additive must have a high specific surface area.

In this work we suggest using $MgAl_2O_4$ spinel as an inert oxide additive. Synthesis of the spinel was done using mechanical activation in a planetary mill AGO-2 from hydroxides as starting reagents with subsequent thermal decomposition. Resulting spinel samples had a high specific surface area (170-250 $m^2/g$). Composite solid electrolytes were synthesized from cesium nitrite and the prepared Mg-Al spinel samples as heterogeneous dopants. The components were mixed and heated at 390 $^oC$. The resulting composite solid electrolytes were investigated by complex of physicochemical methods including X-ray analysis, electron microscopy, chemical analysis, BET adsorption study, etc. Transport properties of composites were investigated in two-electrode cells by the method of complex impedance. The results are discussed in the report.

# REGULARITIES IN THE FORMATION OF COBALT FERRITE WITH A SPINEL STRUCTURE

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In recent decades, the syntheses of spinel ferrites have attracted a great deal of attention due to neutralizing nitrous oxide in the production of nitric acid. Among these materials, cobalt ferrite ($CoFe_2O_4$) possesses high chemical stability, exceptional stability, high mechanical hardness and supports a wide range of applications. The aim of the work is to investigate the influence of precursors on the formation of cobalt ferrite phase and its physical, chemical and catalytic properties. The powders of cobalt oxalate and iron oxalate were used as initial components for mechanochemical synthesis of cobalt ferrite:

$$CoC_2O_4{\cdot}2H_2O + 2FeC_2O_4{*}2H_2O = CoFe_2O_4 + 6CO_2 + 4H_2O$$

The scanning electron microscopy study of cobalt ferrite synthesized according to oxalate technology has shown that the ferrite powder consists of spherical particles. Granulometric analysis has evidenced about logarithmically normal size distribution of particles in the obtained nano-powders of cobalt ferrite, with some inclusions of particles aggregates.

According to X-ray analysis, cobalt ferrite is formed at a temperature below 400°C; a further increase in temperature leads to its crystallization. The sample $CoFe_2O_4$ calcined at 250°C had the highest specific surface (256.1 $m^2/g$), and the least specific surface (10.7 $m^2/g$) was determined in CoFe2O4 calcined at 450°C (see Table 1).

Table 1. Properties of cobalt ferrite.

| | Calcination temperature, °C | | |
|---|---|---|---|
| | 300 | 350 | 450 |
| Specific surface, $m^2/g$ | 256.1 | 117.7 | 10.7 |
| The size of crystallites, nm | 17 | 18 | 30 |

The cobalt ferrite obtained by mechanochemical synthesis has a significant advantage as the catalyst of nitrous oxide decomposition at low temperatures in the production of nitric acid.

# INFLUENCE OF MECHANOCHEMICAL PROCESSING ON FUNCTIONAL PROPERTIES OF ANODE-SUPPORTED MICROTUBULAR SOLID-OXIDE FUEL CELL

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One of directions of alternative energy development is the high temperature electrochemical devices (ECD). Such devices allow to transform effectively organic fuel and hydrogen in electric power with the use of solid-oxide fuel cells (SOFC). Structurally SOFC can be divided into planar and tubular shape. A planar design is widely used in stationary devices, by power from a megawatt and higher, as provides good heat and mass transfer, compactness of assembling and allows to use the standard methods of ceramic treatment. The substantial lack of planar configuration is high requirements to absence of considerable temperature gradients along a membrane, that can result in device destruction during thermal cycling and dramatic changes of temperature. This results in a slow startup speed.

The problem can be solved using microtubular membranes, the advantages of which are improved thermal and mechanical stability, ease of sealing. The rapid launch of high-temperature ECD opens the possibility of developing a promising niche of compact, mobile devices in transport, in the military field and in household appliances.

In this paper, the study of influence of mechanochemical processing on functional properties of anode-supported microtubular solid-oxide fuel cell are presented. The obtained data indicate the promise of mechanochemical processing in microtubular SOFC preparing.

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# SYNTHESIS AND PROPERTIES OF THE HOLLOW FIBER $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ MEMBRANES

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The hollow fiber ceramic membranes based on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) perovskite oxides with mixed ionic-electronic conduction (MIEC) have received considerable attention due to their special advantages for continuous oxygen separation from air. These membranes can be integrated into industrial processes, such as oxy-fuel combustion, partial oxidation of methane into syngas and highly selective oxidation of light hydrocarbons [1]. One of the key factor for excellent membrane synthesis is the preparation of precursor powders via ceramic method. The disadvantage of this method is slow rate of solid diffusion. But the reagents pre-activation with planetary ball mill AGO-2 can be sufficiently force the process rate due to the particle size reducing.

The aim of the work was the synthesis of $Ba_{0.5}Sr_{0.5}Co_{0.8-x}Fe_{0.2}Mo_xO_{3-\delta}$ ($BSCFM_x$) (x=0.02) oxides by ceramic method from $Fe_2O_3$, $Co_3O_4$ and $MoO_3$ oxides, barium nitrate and strontium carbonate with the pre-activation of the starting materials in planetary ball mill AGO-2, the research of BSCFMx hollow fiber membrane morphology developed with phase inversion method, and the study of oxygen permeability of BSCFMx hollow fiber membranes.

According to XRD data, the synthesized $BSCFM_x$ (x=0.02) oxides are single phased with cubic perovskite $Pm\bar{3}m$ structure. SEM images of HF BSCFM2 membranes showed that the membranes have asymmetric structure consisting of finger-like voids originating from both the inner and outer membrane surfaces and central gas-tight layer. BSCFM2 HF membranes are showing high oxygen flux values, the $CO_2$ stability for a long time and the suppression of the oxygen fluxes degradation in the atmosphere containing of 10% $CO_2$.

[1] Sunarso J., Hashim S.S., Zhu N., Zhou W. Progress in Energy and Combustion Science, 61 (2017) 57-77.

# STRUCTURE AND PROPERTIES OF AUSTENITIC STEEL SURFACE-DOPED WITH BORON

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One of the most effective technologies for increasing wear-resistance is surface modification of materials with high-strength particles. The surface hardening of austenitic steel plates, non-vacuum electron beam cladding of powder mixtures on the surface were used. A high-voltage electron accelerator at the Budker Institute of Nuclear Physics, Novosibirsk, Russia, was used for electron beam irradiation. This setup has energy ranges of 1.4 MeV and maximum power of 100 kW. In this study, process parameters were fixed at the optimal conditions (electron energy- 1.4 MeV, specimen moving speed- 10 mm/s, scanning width- 50 mm, beam current- 22-24 mA, and beam diameter-12 mm).The cladded layers, produced uing the aforemetioned regimes, had a thickness of 2.5–3.0 mm. No pores, cracks or delamination were observed.

To estimate the tribological performance of the coating, the wear resistance at friction against fixed and hydroabrasive wear resistance was measured. The wear of steel plates under the impact of a hydroabrasive jet was studied experimentally by varying the angle of impingement of the jet on the plate in the ambient medium (jet in air).

Non-vacuum electron beam cladding is an efficient way for surface hardening of austenitic steel. This technology allows one to produce high-quality cladded layers with thicknesses of 2.5–3.0 mm. The coatings, produced by cladding amorphous boron consisted of 2 different components: $Fe_2B$ and γ-phase (austenite). The microhardness of the coatings was 1.2GPa. The hardening of these coatings was mainly explained due to $Fe_2B$ particles. The cladded layer of samples had the highest wear resistance at all conditions of friction (in 3 times better then austenitic steel).The best wear resistance properties of boron coatings were obtained by cladding at current 23 mA.

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# INVOLVEMENT OF TECHNOGENIC WASTES INTO PROCESSING (MECHANOCHEMISTRY FOR ECOLOGY). PRESENTATION OF THE MONOGRAPH

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The monograph presents the results of long-term studies carried out under the supervision of the author in the laboratories of institutions: Gidrotsvetmet, ISSC&M SB RAS (Novosibirsk), and TIKOPR (Tyva Institute for Exploration of Natural Resources) SB RAS (Kyzyl, the Republic of Tyva).

Original stands were made to implement processing of industrial wastes. The characteristics of the wastes are presented in corresponding sections.

The major value of the entire set of the works described in the monograph is in the cycles that were conducted for every specific object under investigation, from the examination of the characteristics of initial materials to obtaining the commercial products of elevated technological readiness. So, in addition to having solved the problems related to a decrease in the ecological load of industrial wastes on the environment, the economical validity of waste processing is also solved.

The effect of different methods of mechanical, thermal and chemical activation is considered for processing clayey raw materials, arsenic-containing sludge, ash-and-slag dumps of heat and power stations, wastes from asbestos works, dumps and wastes from gold mining. The possibilities and features of mechanochemical technologies for intensification of processing most ecologically dangerous technogenic wastes are demonstrated.

Technological schemes for the recovery of arsenic, nonferrous, rare earth and precious metals, high-purity silicon and magnesium oxides are developed and substantiated (ecologically and economically). Examples of the manufacture of construction, composite and technological materials from technogenic wastes are described, including the fabrication of products and goods of the high technological readiness. The principles of the design of new equipment for the implementation of processes to recover mercury, fine gold and valuable minerals from the dumps of gold mining are substantiated, The results of experimental-industrial development of the technological processes and equipment are described.

# MECHANOCHEMICAL TREATMENT OF OIL SHALE IN SUPERCRITICAL SOLVENT

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It is known that mechanochemical treatment (MT) of solid caustobioliths increases the amount of isolated bitumoids and the yield of light fractions during thermolysis. One can intensify destruction of kerogen - insoluble organic matter of shale - in the process of MT via carrying out it in supercritical fluids.

In this paper the transformations of the organic matter in solid caustobioliths have been investigated during MT in a supercritical $CO_2$ and propane-butane media. The oil shale recovered from the Turhumiy Nuur (Mongolia) deposit containing 13.08 % of kerogen, 0.23% of bitumoid A and 0.26 % wt. of bitumoid B was used as the object under study.

MT was carried out at a rotation speed of 2220 rpm within 5 minutes. MT in argon was carried out under normal conditions and MT in supercritical $CO_2$ and hydrocarbon gases was carried out at the temperature and pressure in the reactor above the critical values of the phases used. The calculated critical parameters were as follows: for $CO_2$ ($T_{crit}$, 31°C, 31°C, $P_{crit}$, 73 atm.); for mixture $C_3H_8$ (65% wt.) - $C_4H_{10}$ (35% wt.) ($T_{crit}$, 111°C, $P_{crit}$, 40.8 atm). The experimental data obtained on the yield of bitumoids are given in the Table 1. It is seen from the data presented that the total yield of bitumoids at MT carried out in propane-butane was 2.3 times greater as compared with the initial shale. MT significantly increased the yield of bitumoid A, with the greatest increase observed when using propane-butane 0.87% wt., When using $CO_2$ the yield of bitumoid A was much less (0.37% wt.).

Table 1. Yields of bitumoids A and B from the oil shale after MT

| MT medium | Yield, % wt. | |
|---|---|---|
| | Bitumoid A | Bitumoid B |
| Argon | 0.66 | 0.27 |
| propane:butane | 0.87 | 0.25 |
| $CO_2$ | 0.37 | 0.29 |

At MT both in the inert and in the supercritical solvent the yield of bitumoid B increased insignificantly.

# TRANSFORMATIONS OF TAR RESINS AND ASPHALTENES MECHANICALLY TREATED AT ELEVATED TEMPERATURES

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At present, the regularities of thermal transformations of petroleum high-molecular compounds are widely studied [1]. It was shown in [2] that during mechanochemical treatment (MT) of tar resins and asphaltenes the processes of destruction and condensation occurred simultaneously, which intensified at MT in the presence of a solid phase. The aim of the investigation is to study the influence of the MT temperature on the regularities of the destruction of tar resins and asphaltenes.

The isolated from tar resins and asphaltenes were mechanochemically treated in argon at 80, 140 and 180 °C for 30 minutes using an AGO-2M unit. Structural-group analyses of the resins and asphaltenes were carried out according to the procedure described in [2].

The compositional analyses of the liquid products indicated that with increasing the MT temperature, the degree of asphaltene and resin destruction increased, resulting in the formation of 11.5 and 10.5 % wt. hydrocarbons (oils), respectively. Structural-group analyses of initial and residual asphaltenes showed that when increasing the MT temperature the structural changes in asphaltene molecules occurred due to condensation reactions leading to an increase in their molecular weight and molecular blocking. Dealkylation reactions intensively proceeded at 180 °C decreasing the number of aliphatic structures in the residual asphaltenes. An increase in the MT temperature of resins enlarged average molecules in the residual resins, although the changes in their structural parameters were insignificant as compared with the initial resins. The asphaltenes formed at the MT of resins were rather large molecules. No direct dependence of the changes in their structural characteristics on the temperature was revealed.

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# PECULIARITIES OF STRUCTURAL CHANGES OF REM-CONTAINING PHASE OF EVDIALITE CONCENTRATE AFTER MECHANOACTIVATION

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Eudialyte is a promising source of medium-heavy and heavy REM, as well as zirconium.

The complexity of processing of eudialyte concentrate (containing in mass %: 56.5 eudialyte ($Na_{12}Ca_6Fe_3Zr_5[Si_3O_9][Si_9O_{24}(OH,Cl)_3]_2$), 14.1 aegirine $NaFe(Si_2O_6)$; 29.4 aluminosilicates) can be provided by a combined method: The 1st stage - Alkaline leaching for selective extraction of silicon into solution and obtaining of a concentrate of rare metals (RM); 2nd stage - Acidic leaching of the 1st stage sediment for extraction RM into the solution.

However, the eudialyte is resistant to alkaline solutions. In connection with this, short-term mechanoactivation (MA) was used to increase the reactivity of the eudialyte. The Fig. 1 shows photomicrographs of eudialyte concentrate after MA (1 - eudialyte, 2 - aegirine).

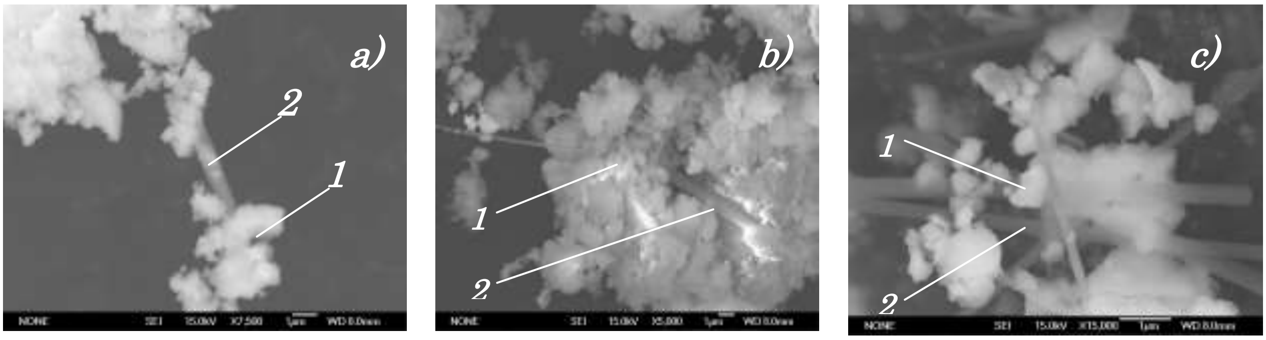

Fig. 1. Microphotographs of eudialyte concentrate after MA in the planetary ball mill (LAIR-0.015) at $M_b$: $M_k$ = 80: 1: a) $\tau_{MA}$ = 2.5 min; 25 g; b) $\tau_{MA}$ = 5 min; 25 g; c) $\tau_{MA}$ = 5 min; 35 g, a magnification 7500x, 5000x and 15000x, respectively.

The preservation of the morphological heterogeneity of the eudialyte concentrate after MA has been established even in a state close to the X-ray-amorphous concentrate. This ensured the selectivity of silicon recovery from the eudialyte phase during alkaline leaching.

# AFFIRMATION OF THE METHODS TO GOVERN STRUCTURE IMPERFECTION AND DISPERSITY OF MINERALS DURING THEIR SELECTIVE DESTRUCTION

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Urgent direction in broadening the mineral raw material basis is involvement of finely impregnated, unyielding difficultly concentratable ores, and technogenic objects. The central problems in this direction are low-defect selective grinding of mineral associations and minimization of the formation of micron-sized slime particles not amenable to separation and concentrating. It follows from the analysis of mineral destruction mechanisms that one of the major conditions for improved treatment of crystalline aggregates should be considered to be an increase in the energy of mechanical action.

Highly stressed free shock implemented in integrators is the most suitable condition meeting the requirements. This shock allows not only to minimize the formation of defects and slime but also to destroy the matrix of the ore body selectively by isolating the fragments of different strength.

New possibilities in decreasing the imperfection and the size of micron-range particles are opened in the case when minerals are destroyed in the presence of surfactants. Their action is considered from the viewpoint of the grease effect which decreases the friction coefficient and the residual deformation of the surface structure of minerals. Traditional floatation collector agents, including poorly soluble nonpolar substances. The application of a combination of reagents providing both chemical and physical sorption of substances is the most successful approach. The action of the surfactants decreases amorphization of mineral surface during grinding in centrifugal planetary mills. Especially important advantage is a decrease in slime formation; the amount of particles less than 10 micrometers decreases to 40 %, which causes a substantial increase in the qualitative and quantitative parameters of concentrating processes.

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# TRIBOTECHNICAL CHARACTERISTICS OF MECHANOACTIVATED THIN COATINGS

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Mechanochemical technologies are also effective in the preparation of composite thin film based on fluorine-containing compounds. The main method for their implementation is mechanoactivation when mixing components in a blade or anchor mixer under controlled parameters of the effect of elements on a powder mixture. In the technology of composites based on PTFE, it is necessary to emphasize the possibility of inversion of certain features of the structure of the polymer matrix, adversely affecting the wear resistance, manufacturability, strength, in the positive factor of increasing service parameters. Among such features it is necessary to attribute the possibility of destruction of the block of polytetrafluoroethylene (PTFE) under the influence of small tangential loads with the formation of dispersed fragments with a large number of macro radical products. Therefore, it seems to us that one of the ways to increase the indices of tribotechnical and technological characteristics of PTFE coatings can be realized with the directed use of processes of mechano-tribo-cracking of the matrix component or modifiers at various stages of the process of formation and application of materials. Obvious is the assumption of the need to incorporate into the composition of PTFE-based ingredients that activate the mechano- (tribo) cracking processes and ensure the interaction of the products formed with other components in the process of forming the structure of the optimal structure. The analysis of literature sources and the results of the conducted studies indicate the effectiveness of using mechanochemical reactions at various stages of the formation of composite materials based on polytetrafluoroethylene and the application of coatings from them in friction units. Of particular interest are reactions involving radical products formed during thermo- mechanocracking of polymeric and oligomeric components of fluoroplastic compounds.

# MECHANICAL PROPERTIES OF CERAMIC MATERIAL OBTAINED BY SPARK PLASMA SINTERING

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It is known that ceramic materials possess unique physico-mechanical, tribological properties and displace in practice a number of alloys with a similar purpose. The investigated silicon carbide material was obtained using secondary industry products as initial components. The sintering was carried out by spark-plasma method with a Labox unit. The sintering regimes are indicated in Table 1.

Table 1. Initial chemical composition of powders and sintering parameters.

| № | Sample name | T sintering, $^0$C | Time excerpts, min | Heating rate, ºC/мин | Load, kH | Chemical composition, mass% | |
|---|---|---|---|---|---|---|---|
| | | | | | | Si | C |
| 1 | SiC-1 | 1600 | 5 | 100 | 12 | 75 | 25 |
| 2 | SiC-2 | 1400 | 5 | 100 | 12 | 75 | 25 |
| 3 | SiC-3 | 1200 | 5 | 100 | 12 | 75 | 25 |
| 4 | SiC-4 | 1500 | 5 | 100 | 12 | 75 | 25 |
| 5 | SiC-5 | 1300 | 5 | 100 | 12 | 75 | 25 |

The coefficients of friction and wear resistance of the obtained samples of ceramic material were determined. The results are shown in Table 2.

Table 2. Friction coefficient of the samples and the wear rate

| № п/п | Sample name | Friction coefficient | Wear rate, $10^{-6}$ |
|---|---|---|---|
| 1 | SiC-1 | 0,618 | 1,56 |
| 2 | SiC-2 | 0,601 | 34,6 |
| 3 | SiC-3 | 0,680 | 11,3 |
| 4 | SiC-4 | 0,256 | 0,92 |
| 5 | SiC-5 | 0,651 | 13,7 |
| 6 | Prototype | 0,326 | 0,24 |

It is established that all samples obtained by the spark-sintering method have a low coefficient of friction and are wear-resistant. As the sintering temperature of the samples increases, the coefficient of friction decreases.

# INFLUENCE OF THE GLASS SUBSTRATE TREATMENT BY SURFACE ION EXCHANGE AND CHEMICAL ETCHING ON STRUCTURAL FEATURES OF THE GOLD NANOLAYER

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The research data are related to X-ray structure analysis of the Au nanolayers (50, 100, 200 nm thick) on glass substrate surface modified by the surface $Na^+/Li^+$ ion exchange, chemical etching or by treatment combining two indicated above methods. The soda lime silica glass substrate has been modified by the special Surface Ion Exchange Paste (SIEP) [1-3] at ~ 300º C (15 – 20 min.). The chemical etching has been carried out with the composition containing HF acid [4]. The surface morphology was observed by the SEM JSM-6460 (Jeol, Japan); Au nanolayers were deposed by device JVC-1600 (Jeol, Japan). X-ray data were measured with diffractometer D8 Advance ($CuK_\alpha$ radiation) and one-dimensional detector Lynx–Eye (Ni filter); the program Topas 4.2 and initial structural data ICSD have been used. X-ray data analysis allows make conclusion that the glass surface modification by the surface ion exchange and chemical etching have a substantial influence upon the size of Au crystal grains (Fig.1) having elongated shape in direction <111>. Increase of the Au nanolayer thickness leads to decreasing of the crystal grains size. The least size have been related to Au nanolayer 200 nm thick on glass surface modified by combined method indicated above: in direction <111> average calculated grains size (A1, Figure 1) is ~ 14.7 nm; grains size averaged in directions <200>, <220> and <311> (B1, Fig.1) is ~ 6.8 nm.

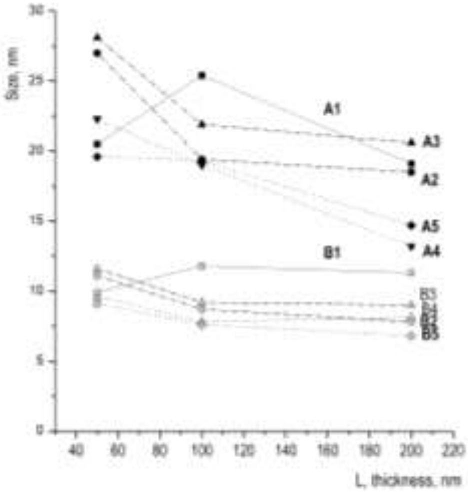

Fig. 1. Size of gold crystal grains in dependence on Au nanolaver thickness.

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# MECHANOCHEMICAL TECHNOLOGY OF PRODUCTION OF NOVEL GYBRID MATERIALS FOR OIL INDUSTRY

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Hybrid materials result in combination of functional polymers with inorganic structures. Such materials have often a nano-structural composite structure and nano-dimensional inclusions can be both particles and fibers of the corresponding size. As a result of such combinations the received materials have unique physical and chemical properties which either completely are absent, or only partially present in parental materials. There are many methods of hybrid materials production for the moment. Mechanical mixture of powders, zol-gel methods, emulsion polymerization and photo polymerization are most known. Besides, synthesis of hybrid composites approaches of supramolecular and coordination chemistry are used, combine chemical synthesis with ultrasonic and high-frequency processing. During more than 10 years we develop mechanochemical methods of receiving such hybrid materials and their use in oil-field practice. As feed stock for production of such materials we serve cheap natural minerals and materials, fulfilled catalysts or metallurgical slime, agricultural waste.

The first nanostructured material - the silicate gel received from river sand - has been made and tested on the Sredne-Asomkinsky field more than ten years ago. For reinforcement of obtaining gel we have used fine sand of 0,1 in size – 40 microns. Synthesis of gel was carried out by neutralization of alkaline sand suspension in the well.

Inorganic gels have high mechanical properties but are fragile and after excess of some threshold of critical tension they are irreversible collapse. These shortcomings organic gels are deprived, but they, in turn, have a low limit of fluidity. Organic gels are deprived of these shortcomings, but they, in turn, have a low limit of fluidity. The rice peel contains up to 20% of amorphous silicon dioxide and up to 35% of cellulose and it is possible to synthesize carboxymethyl cellulose and silicate of sodium from this material under certain conditions. The new organo-inorganic materials produced of rice husk have shown a combination of elastic and plastic properties, which are absent in separately obtained silica gel and carboxymethyl cellulose.

Some new cheap hybrid organo-inorganic materials from sand and peat have been also produced and investigated. Rheological curves of the mixed materials differ from the initial ones and show the new properties which are absent in separated initial materials. So, gel on the basis of composition shows viscous and elastic properties that allows to use it for creation of temporary screens for redirection of water streams when carrying out repair work. This method also for carrying out irrigation amelioration and against floods in megapolises.

So, gel on the basis of composition shows viscous and elastic properties that allows to use it for creation of temporary screens for redirection of water streams when carrying out repair work. This method is also promising for carrying out irrigation amelioration and against floods in megapolises.

# STRUCTURE AND PROPERTIES OF NBC DOPED AUSTENITIC STEEL

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Austenitic steels are widely used in different industry fields, but the range of application is limited due to low wear resistance of these steels. One way to increase surface strength and wear resistance is coating formation. Nowadays, the high-energy methods of surface treatment are promising. In this study, we used the electron beam cladding technology at the atmosphere for increasing the surface strength of austenitic chrome-nickel steel. Specialists of the Institute of Nuclear Physics (Siberian Branch of the Russian Academy of Sciences (SB RAS) Novosibirsk) have developed industrial electron accelerators type ELV-6 which characterized with high efficiency, the maximum power reaches 100 kW. The regimes of cladding were following: accelerating voltage was equal to 1.4 MeV; a beam current of 22, 23 and 24 mA was used. The distance from the outlet window to the working surface is 90 mm, a beam diameter was 1.2 cm. The oscillating amplitude of a beam was 50 mm, the velocity of sample movement relative to the electron beam was 1 cm/s. The choice of regimes was based on papers and investigations of specialists of the Institute of Nuclear Physics. The mixture of niobium carbide, flux ($MgF_2$) and iron (as wetting agent) powders was used for cladding. The X-ray analysis, optical and scanning electron microscopy were used to investigate the formed structure. The obtained coatings have thickness ~1.8 mm, good adhesion to substrate; there are no pores and cracks in the structure. The coatings structure consists of austenite with distributed niobium carbides. The microhardness of samples ~400-450 HV that’s twice as much compared to austenitic steel.

Hereafter it’s planned to investigate the structure of formed coatings using transmission electron microscopy and also to carry out the fixed abrasive particles test, test on hydroabrasion wear and test on gas abrasion wear.

The work was financially supported by the Ministry of Education and Science of the Russian Federation (Agreement No. 14.610.21.0013, project identifier RFMEFI61017X0013).

# THE EFFECT OF MECHANICAL ACTIVATION ON THE CORROSION RESISTANCE OF THE $NI_3AL$ INTERMETALLIC, OBTAINED BY SPS

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Recently, spark plasma sintering (SPS) technology of aluminides has become increasingly widespread. $Ni_3Al$ is the basis of modern high-temperature alloys designed for operation under extreme conditions of thermal and power loads. In this paper, the preforms were obtained by sintering of the nickel and aluminum powders at a temperature of 1100 °C in order to form the $Ni_3Al$ phase with preliminary 3 minute mechanical activation and without it. Corrosion resistance of sintered materials was evaluated by the weight method in a solution of 5% sulfuric acid heated to 50 °C. Tests were conducted for 5 hours. The corrosion rate of intermetallic materials was compared with the commercially pure components - aluminum and nickel (obtained by SPS).

The carried out experiment showed that the highest value of the corrosion rate was recorded on an aluminum sample, which was 5.6 mm/year. The immersion of a sample from nickel under similar conditions indicates a higher level of corrosion resistance of the material. The dissolution of the metal under the action of the medium occurred at a rate of 1.4 mm/year. The lowest value of the corrosion rate was established for the intermetallic $Ni_3Al$. The corrosion ratio of such a composition was ~ 0.9 mm/year and, as a rule, does not depend on additional mechanical activation of the powder mixtures before sintering.

After corrosion tests, the surface of the materials studied was analyzed by scanning electron microscopy. It was found that aluminum is subject to general corrosion. For nickel samples and $Ni_3Al$, after mechanical activation of powders, the traces of abrasion is maintained at the preparation stage. For samples with preliminary mechanical activation, corrosion develops evenly over the entire surface area. The exclusion of mechanical activation of powder mixtures at the initial stages leads to a selective etching of the material in the solution, which is due to a lack of uniform distribution of the particles in the powder mixture.

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# FORMATION OF STRUCTURE AND PHASE COMPOSITION OF NI-BASE ALLOYS OBTAINED BY HIGH-SPEED DIRECT LASER DEPOSITION

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Additive manufacturing (AM) is new technologies for production components with complex geometry directly from CAD model by layer-by-layer manner. Nowadays one of the most promising type of AM is direct deposition, since the use of this type is applied not only to create products with complex geometry, but also can be used for recovering operations of worn parts of products.

The structure and phase composition of products created during AM has some features that influences on final mechanical properties of materials. Usually the dendrite structure is formed during AM, but high-speed direct laser deposited has a specific process of powder transfer which leads to a bulk crystallization of the material, which has a better mechanical property than the cast structure. The samples obtained with the low laser power contained incompletely molten particles of the initial powder with border pores. On increasing the laser power there is structure with the growth of grains from the centers of the powder particles. Such areas indicate the occurrence of bulk crystallization. And the structure with highest laser power has oriented growth direction of dendrites.

One of the strengthening mechanisms of nickel-base alloy is precipitating ($\gamma'$-phase, carbides), the main benefit of which is achieved by heat treatment. Since layer-by-layer production creates repeated heat-effect areas, it can be considered as heat treatment on material. Depending on regimes of heat treatment the different volume, composition and shape of the strengthening particles are formed and hence the different effects on mechanical properties are created.

It was observed that the arrangement order of precipitating $\gamma'$-particles, located into the fcc solid solution of nickel matrix, is changed in accordance with the various laser power. The as-deposited samples obtained with the medium laser power have the ordered positions of precipitating particles. And the as-deposited samples manufactured with the minimum and maximum laser power have the unordered positions of particles corresponding to the untreated material. Thus, the samples obtained at the medium laser power have a material structure that does not require additional heat treatment.

# INTERMEDIATE STATES IN GLYCINE - MALONIC ACID - WATER SYSTEM

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Mechanical treatment of crystalline powder mixtures has been reported in numerous publications to produce new compounds. Mechanochemical processing of dry powders is usually referred to as neat grinding, as opposed to more popular technique of liquid-assisted grinding (LAG). The assumption of neat mechanochemical conditions must, however, be made with caution even if the reactants are not crystal hydrates, since the role of atmospheric moisture cannot immediately be neglected. We illustrate this by using the "dry" mechanochemical reaction between glycine and malonic acid in various atmospheric conditions as an example. The mixture of α-glycine and malonic acid is shown to be highly hygroscopic even at ambient conditions. Dissolution of reactants in adsorbed atmospheric moisture is observed at the macroscopic level and demonstrated to be sufficient to cause spontaneous and crystallisation of the salt product. Formation of several low-crystalline hydrate compounds was also registered, followed by dehydration and further decomposition. Such fluidised intermediate states, which are required in many cases for mechanochemical organic co-crystallization, can be easily produced by reactants' mixture interacting with atmospheric moisture during mechanical treatment.

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# THE INFLUENCE OF MECHANOCHEMICAL ACTIVATION OF THE MEDICINAL PLANT MATERIAL ON THE YIELD OF WATER-SOLUBLE SUBSTANCES

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The increase of yield of extractive and active substances obtained from the plant material is one of the most important problems in the technology of traditional medicinal preparations.

In this work the influence of the mechanochemical activation on the yield of water-soluble substances obtained from three species of the medicinal plant material, namely, the leaves of *Bergenia crassifolia (L.) Fritsch.*, leaves of *Rhododendron aureum* and roots of *Scutellaria baikalensis Georgi* was studied.

Mechanochemical activation of the specimens was carried out with a planetary centrifugal ball mill of AGO-2 type for 2 minutes; 10 g of the mixture of raw material and supplement together with 200 g of balls were charged into a shell of the mill. $Na_2CO_3$, NaOH, sugar, $H_3PO_4$, ascorbic acid, cellolytic enzime cellolux, protolytic enzime protosubtilin were used as supplements.

Specimens for comparison were ground up in the cutting mill MRP-2 to the size of particles passing through the 2 mm sieve size.

The quantity of water-soluble substances was determined with the use of the Soxhlet apparatus-like device under reflux. The yield of water-soluble substances (mas. %) was determined according to the mass of dry extract as well as according to the mass of sediment, washed free of water-soluble substances and dried at $60^0$ C.

Maximum increasing of the water-soluble substances yielded during mechanochemical activation of the *Bergenia crassifolia* and *Rhododendron aureum* leaves and *Scutellaria baikalensis* roots amounted to 22% (supplement – 5% $H_3PO_4$), 35% (supplement – 5% $Na_2CO_3$) and 66% (supplement – 1% cellolux) respectively.

From our point of view, the choice of mechanochemical reagent for maximal extraction of plant raw is dependent upon the nature of raw and nature of extracted substance and must be defined by results of previous experiments with alkali, acid, enzime character.

# ANTI-CORROSIVE FACING ALLOY FOR RESTORATION AND PROTECTION OF SUBMERSIBLE PARTS OF OIL-PRODUCING EQUIPMENT

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The preparation of surfacing materials by the method of mechanical alloying is suggested. The use of mechanochemical technology allows to exclude energy-consuming technological operation - thermal processing of powder material. The method of mechanical alloying makes it possible to obtain surfacing powder materials, which can not be obtained in the usual way, and also allows to obtain required composition of powder surfacing materials without restrictions on number of components, compounds of different chemical composition, melting temperature of components and their physicochemical properties [1].

The combination of the method of mechanical alloying with the conglomeration of the obtained powder mixtures allows creating various compositions of the welding alloy providing high-quality coatings.

The paper presents a prototype sample of a new anti-corrosion, wear-resistant surfacing alloy applicable for formation of protective coatings to parts of submersible oil-producing equipment. The welded new powder surfacing alloy with chemical composition (mass.%): carbon - 1,1-1,4; silicon - 2.0 - 3.0; manganese - 0,9 - 1,4; chromium - 14.0 - 15.0; nickel - 30.0 - 32.0; titanium 1.0 to 1.1; tungsten - 2.5 - 2.9; vanadium 3.0 to 4.0; copper - 3,0 - 4,0; boron 2,0-2,9; iron-32.0-40.0, is resistant to corrosion in aggressive media (30% and 60% solutions of H2SO4).

The analysis of the results of corrosion tests in an aggressive environment (H2SO4), containing more than 30% of nickel and about 15% of chromium, allows us to attribute the investigated protective coating to a group of persistent ones. According to physicochemical parameters, the proposed anticorrosive surfacing alloy will surpass competitors as it will be oriented to existing corrosion problems. The cost of the alloy also will be lower than this of competitors due to use of domestic components of the alloy and low industrial expenses. Moreover the technological process does not require huge production area and the harm to the environment is not significant.

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# 3D PRINTING OF SODIUM ALGINATE AND PECTIN A-MIN HYDROGELS. DETERMINATION OF 3D PRINTING PARAMETERS

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Using a method of 3D printing in a special supporting suspension (Figure 1), the samples from the sodium alginate and pectin A-min hydrogels were obtained. Calcium chloride, gelatin type P-11 and distilled water were used to prepare the supporting suspension. To identify the optimal composition of the supporting suspension, a method for its preparation and concentration of hydrogel components was developed. The possible ranges of material extrusion speed for 3D printing of the outer perimeter and extrusion speed for printing the internal filling of the model with using 2.5% sodium alginate hydrogel were determined. The movement speed of the print head when printing the outer perimeter of the model with 3D printing 2.5% hydrogel of sodium alginate was experimentally established. The optimal concentration of pectin A-min in the hydrogel for 3D printing is 8%.

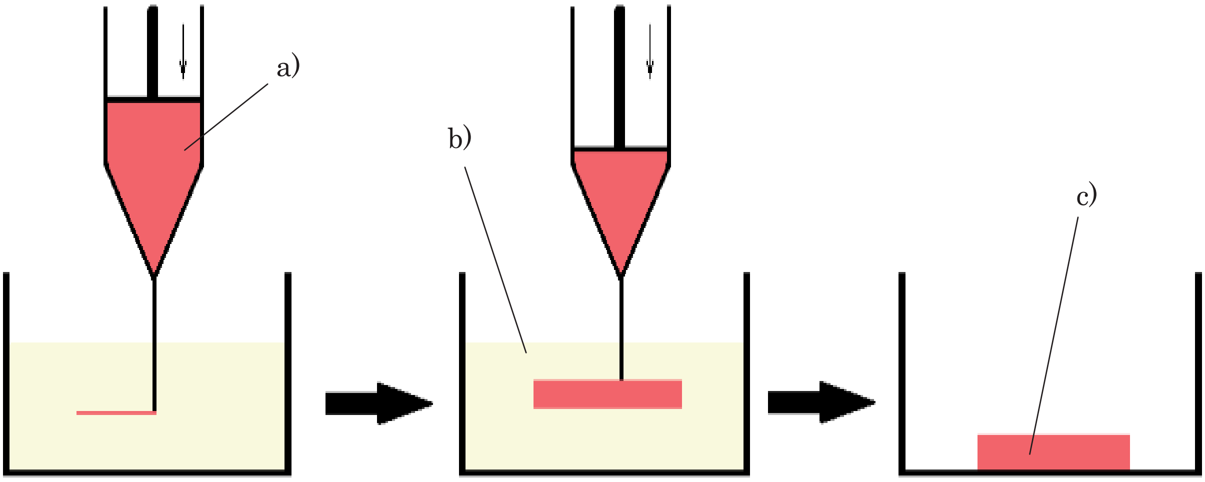

Fig. 1. The scheme of obtaining objects from the hydrogel by the method of 3D printing a) sodium alginate hydrogel in a special extruder, b) supporting suspension, c) printed object from the hydrogel.

# THE EFFECT OF MECHANOCHEMICAL ACTIVATION ON THERMAL SYNTHESIS IN MIXTURES BASED ON METAKAOLIN AND SODIUM HYDROXIDE

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It was investigated the thermal behavior of the mixtures $6Al_2Si_2O_7$: 12NaOH and $6Al_2Si_2O_7$: 12NaOH: $2Al_2O_3$ which are designed for synthesis of LTA zeolite. Roller-ring vibration mill VM-4 has been used for preliminary mechanical activation of dry mixtures. It was found that after evaporating suspensions, molding pellets and drying, small amounts of LTA and sodium hydroaluminates have been formed in the sample. The removal of crystallization water occurs on heating up to 400°C. In the temperature range from 400 to 850°C, $Na_6Al_4Si_4O_{17}$ and $Na_8Al_4Si_4O_{18}$ are synthesized by interaction of metakaolin with sodium hydroxide. The formation of mullite and nepheline is observed also. For the range 400–850°C, the values of apparent activation energy and pre-exponential factor have been calculated using Ozawa–Flynn–Wall analysis. It was shown that pre-activation of powders in the vibratory mill allows reducing the starting temperature of synthesis on 50–100°C as well as decreasing the apparent activation energy on 50–150 kJ/mol. Also it was shown that alumina excess inhibits nepheline and mullite formation.

The reported study was funded by RFBR according to the research project No. 16-03-00163 A.

# INFLUENCE OF CO-GRINDING ON THE KINETICS OF THERMAL DECOMPOSITION IN THE Z/Al(OH)$_3$ MIXTURES (Z = ZnO or Zn$_4$CO$_3$(OH)$_6$·H$_2$O)

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The kinetics of non-isothermal decomposition of ZnO/Al(OH)$_3$ and Zn$_4$CO$_3$(OH)$_6$·H$_2$O/Al(OH)$_3$ has been studied both for the starting mixtures and for mixtures after co-grinding. The process has been controlled by X-ray diffraction, scanning electron microscopy, thermogravimetry and differential scanning calorimetry under air atmosphere (the heating rates were 5, 10 and 15 °C min$^{-1}$). The activation energy was calculated using the Friedman and Ozawa–Flynn–Wall analysis. It was shown that both methods gave similar results. It was found that the dehydration activation energy of gibbsite to boehmite in the mixture with ZnO gradually is decreased from 150–170 to 100 kJ mol$^{-1}$. At the final stage (conversion degree was more than 0.9), the dehydration process converted from kinetic mode into the diffusion mode (the activation energy was 50–70 kJ mol$^{-1}$). It was established that the activation energy of Zn$_4$CO$_3$(OH)$_6$·H$_2$O/Al(OH)$_3$ decomposition at a conversion degree less than 0.5 (decomposition of basic zinc carbonate to ZnO) has values 130–170 kJ mol$^{-1}$. For a conversion degree 0.5–0.9 (dehydration of gibbsite to boehmite) the activation energy amounted to 90–130 kJ mol$^{-1}$. At the final stage of decomposition (degree of conversion above 0.9), the process occurred in the diffusion mode in which the activation energy amounted to 40–70 kJ mol$^{-1}$. It was revealed that after co-grinding of the ZnO/Al(OH)$_3$ composition, the dehydration process activation energy has decreased by 10–20% compared with the original mixture. After the co-grinding of Zn$_4$CO$_3$(OH)$_6$·H$_2$O/Al(OH)$_3$ mixture, the activation energy has increased by 10–15%. These facts had been explained by changes in the size and defectiveness of the solid phase particles.

# MECHANOACTIVATED SYNTHESIS OF ALUMINIUM BORON CARBIDE

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Aluminum boron carbide $Al_3BC_3$ has low density (2.66 g/cm$^3$), high hardness (18.2 – 20.7 GPa) and excellent oxidation resistance. As the melting point of $Al_3BC_3$ is 1835 °C, it can be used as sintering additive to SiC or $B_4C$. The synthesis of $Al_3BC_3$ through carbo-thermal reduction requires temperature of 1725 ºC (4 h) - 1800 ºC (1 h) [1]. Such a high temperature leads to intensive evaporation of the volatile suboxides AlO, $Al_2O$ and $B_2O_2$. In the present study the effect of ball-milling on the temperature of $Al_3BC_3$ formation was investigated. The $Al_3BC_3$ synthesis was carried out in vacuum at T = 1500 ÷ 1850 ºC during isothermal exposition of 2 h according to the reaction:

$$3Al_2O_3 + 2H_3BO_3 + 7C \rightarrow 2Al_3BC_3 + 3H_2O\uparrow + CO\uparrow + 5{,}5O_2\uparrow$$

The ball-milling and mechanoactivation of $Al_2O_3$-$H_3BO_3$-C mixture were carried out in the laboratory attritor Union Process HD-01 with $Al_2O_3$ grinding tank and $Al_2O_3$ balls (3 mm diameter) in distilled water with 1 % of isopropanol as a surfactant. Milled and synthesized powders were analyzed using XRD (Fig.1), EDX and laser diffraction in liquid. The temperature of $Al_3BC_3$ complete formation was determined. The decrease in the temperature of synthesis was more than 200 ºC for mixture milled at 24 h /500 RPM.

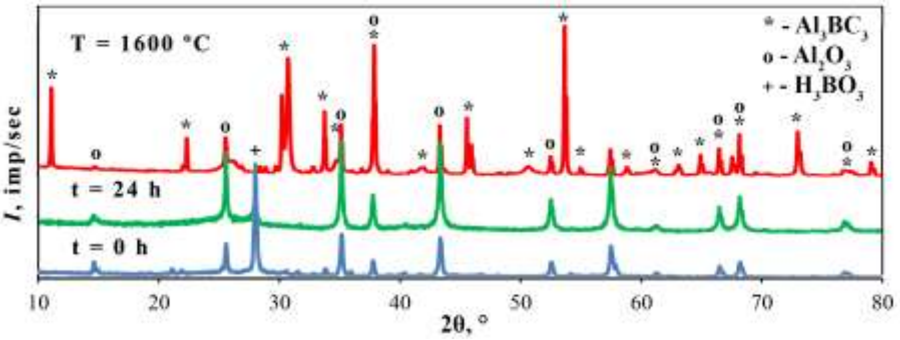

Fig. 1. XRD spectra of $Al_2O_3$-$H_3BO_3$-C milled at 400 RPM and synthesized at 1600 ºC.

The reported study was funded by RFBR (research project No. 17-03-00863\18).

[1] Lee S. H., Yin J., Feng L., et al. J. Ceram. Soc. Jpn. 122, No.1429 (2014) 772-776.

# FORMATION OF AN EXTENSIVE DIFFUSION ZONE ON THE EXAMPLE OF BINARY SYSTEMS TiAl AND NiAl

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Investigation of the diffusion zone at the interface of nickel/aluminum and titan/ aluminum carried out in this paper. The bimetallic samples, which are a pressed plate of nickel, aluminum and titan, aluminum, were annealed in a vacuum furnace at a temperature above the melting temperature of aluminum. Formation of diffusion zones were investigated using the specimens after different time of annealing. Sintered samples were cut across the boundaries of the section; the cut surface was planished and polished.

Analysis of experimental results suggests that the increase in time of thermal activation of diffusion processes leads to an increase in the width of the diffusion zone for which the measured micro hardness is a function with a maximum that indicates the nature of the distribution of the phase components at the interface nickel/aluminum and titan/aluminum. As it follows from the phase diagrams of Ni-Al and Ti-Al, the most wide homogeneity range, and, consequently, greater probability of formation of intermetallic compounds are characteristic of phases NiAl, $Ni_3Al$ and TiAl, $TiAl_3$, respectively.

The diffusion zone at the interface of bimetal nickel/aluminum and titan/aluminum is a macroscopic object, testifying thereby about macroscopic diffusion distance of diffusants.

Measured diffusion parameters of the diffusion zone at the interface of bimetallic sample suggest that with increasing time of exposure at 700 $^0$C the diffusion coefficient increases. The increase in co-factor of the diffusion is apparently due to the formation of branched intergranular and interphase boundaries during the synthesis of intermetallic compounds in the diffusion zone. The combination of intermetallic phases and solid solutions determines the strength properties of the diffusion zone, and, consequently, the adhesion strength of the bimetallic unit.

# SOLID-PHASE CONVERSION OF URANIUM TETRAFLUORIDE USING QUARTZ MECHANOACTIVATED IN PRESENCE OF ALKALINE ELEMENTS SALTS

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In scope of "The concept of safe treatment of depleted uranium hexafluoride ($DUF_6$)" working now, the storage of $DUF_6$ in steel containers situated in open stockpile sites that is presently in use is potentially accidental and associated with overbalance of significant amounts of fluorine. Conversion of $DUF_6$ into a form more easy-to-use, e.g. – into oxides, seems to be a possible solution of this problem. The process can be carried out resulting in production of high-purity fluorides as co-products. For example, a two-stage conversion – initially into $DUF_4$ leads to formation of HF or organic fluorides, while the second stage results in oxides. This stage involves mechanically activated quartz in presence of promotive additives (PA), e.g. NaF и $Na_2CO_3$ [1]. In nooxidizing medium, at low temperature and under conditions of removal of a gaseous product of the reaction maintained in our study a formation of sodium fluoro-uranates in $UF_4$ – $SiO_2$(PA) system has been observed. The effect of various PAs (LiF, KF, $Li_2CO_3$, $K_2CO_3$) on reactivity of mechanically activated quartz estimated with respect to the conversion process, which was conducted under the same conditions, has been studied. The experimental conditions were described in [1]. Phase compositions of the samples obtained at 400-600°C temperature range were determined using D2 PHASER device.

The dependencies of the conversion efficiency on temperature and PA concentration have been found actually the same as for NaF. It has been confirmed that the interaction in $UF_4$ – $SiO_2$(PA) system started from the reaction of $UF_4$ with a PA (at 400°C $M_7U_6F_{31}$ and $UO_2$ phases were observed). By the increase of temperature up to 500°C and 550°C a formation of fluoro-uranates of $Li_3UF_7$ ($K_2UF_6$) и $Li_4UF_8$ ($K_3UF_7$) occurred. The reaction product – $UO_2$ obtained at 600°C contained small amounts of LiF (KF), which can be readily removed. Thus, it is possible to conclude that the compounds of alkaline elements studied catalyze $UF_4$ into $UO_2$ conversion in the same way as NaF and $Na_2CO_3$.

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# MECHANOCHEMICAL PROCESSES DURING VIBRATION PROCESSING OF TITANIUM IN THE PRESENCE OF POLYMER

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The processes of mechanical activation of titanium powder jointly with the destructible polymer in a vibratory mill were investigated.

The titanium powder of PTES-2 grade with a dispersion of 150-200 μm and purity of 99.8% was used. The emulsion of polymethylmethacrylate (PMMA) was used as a solid high-molecular compound. The activation of the initial components was carried out in the vibratory mill at a container oscillation frequency of 750 min$^{-1}$ and amplitude of 90 mm. for 5-45 min. The PMMA content of the processed composition was from 1 to 15 wt.%. X-ray phase analyses (XPA) of the synthesized materials were carried out with D8 Advance diffractometer (Germany).

It was revealed that at a certain content of the polymer, a jump-like increase of temperature of external walls of the mechanoreactor was observed during vibrating treatment of the "Ti + PMMA" mixture. No jump-like increase of temperature was observed up to 45 minutes of processing when polymer content was less than 3 and more than 9 wt.% in "Ti + PMMA" system. The minimum activation time of the "Ti + PMMA" composition before the jump-like increase in the temperature of the mechanoreactor corresponded to the polymer content of 5 wt.% (15 min) and maximum of 9 wt.% (30 min). At polymer content from 10 up to 14 wt/%, the jump-like temperature increase was not observed, however, along with titanium its carbide, nitride and hydride have been found in the final product according to XPA data.

Thus, the vibrating treatment of the powder composition "Ti + PMMA" at the polymer concentration from 3 up to 9 wt.% initiates mechanochemical reactions accompanied by a significant exothermic effect. The product of mechanochemical reactions is a powder composition consisting of titanium and its carbide, nitride and hydride. The optimal polymer content for implementation of mechanochemical synthesis involving titanium and products of mechanical and thermal destruction of high molecular compound is 5 wt.% of the amount of metal being processed.

# THE INFLUENCE OF CHEMICAL AND MECHANICAL PREHISTORY ON THE GAHNITE SYNTHESIS

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Zinc aluminate $ZnAl_2O_4$ (gahnite) is a mineral from the spinel group. It is the only compound that is formed in the system $ZnO – Al_2O_3$. The gahnite is used in various catalytic processes, as the second phase in a glaze for white ceramics, as a component of a luminescent coating, etc.

The data obtained for the zinc spinel accumulation in some original substances interaction may be described satisfactorily by Ginstling-Brounshtein equation:

$$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=k_{ГБ}\tau\ ,$$

where $\alpha$ – conversion degree expressed as a decimal fraction; $k_{ГБ}$ – effective rate constant, $sec^{-1}$; $\tau$ – time, sec.

The calculated rate constants are presented in the Table 1.

Table 1. Effective rate constants for $ZnAl_2O_4$ formation.

| Precursors | Effective rate constant $k_{ГБ}\cdot10^5$, $sec^{-1}$ |
|---|---|
| $ZnO + Al_2O_3$ | 3.5 ± 0.5 |
| $ZnO + Al(OH)_3$ | 20 ± 1 |
| $Zn(OH)_2 + Al(OH)_3$ | 34 ± 3 |
| $Zn(CH_3OO)_2 + Al(OH)_3$ | 49 ± 7 |

Oxides interact with the minimal rate as compared with hydroxides and a salt. By all appearances, at the last cases mentioned above the Hedwall effect becomes apparent. The increased chemical substances activity under some crystal reconstruction goes a long way for reactions in which alumina compounds take part because of the complicated $Al_2O_3$ polymorphism.

The influence of a mechanical activation and microwave pretreatment of the reactive mixture on the compounds interaction rate has been appreciated by means of IR-spectroscopy, X-ray phase analysis and kinetics data.

# THE ACTIVATED SYNTHESIS OF MULLITE

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The mullite $3Al_2O_3{\cdot}2SiO_2$ is an inorganic material that has a tremendous significance for the technology of high-temperature and chemically stable products.

Hydrated oxides obtained in an active form because of mechanical activation or coprecipitation (precursors) were subjected to a high-temperature treatment (800-1400 $^oC$). A mechanical activation of $Al(OH)_3$ + $H_2SiO_3$ was carried out in AGO-2 planetary mill. The components were premixed in the ratio $Al_2O_3:SiO_2=3:2$. In the part of experiments the white sintered mullite was used as seed crystals ("Cermatco"). The mullite-forming suspension was obtained by the coprecipitation of hydrated oxides forms with the help of carbamide.

The solid-state synthesis kinetics of the mullite from aluminum hydroxide and metasilicic acid has been studied. The reaction rate was described by the kinetic first-order equation:

$$K_T = \frac{1}{\tau} ln \frac{a}{a-x},$$

where, $K_T$ – effective rate constant, $sec^{-1}$; $\tau$ - time, sec; $a$ – initial $Al_2O_3$ content in the mixture, %; $x$ –$Al_2O_3$ quantity that has entered into the reaction, %.

Energy activation values were determined (Table 1). The positive role of mullite seed crystals (0.1 %) in the product accumulation was confirmed.

Table 1. Mullite-forming reaction kinetics parameters.

| Used precursors | Activation energy, kJ/mole |
|---|---|
| Base mixture with no mechanical activation | 350 ± 40 |
| Base mixture after the mechanical activation in the planetary mill | 280 ± 10 |
| Base mixture after the mechanical activation in the planetary mill in the presence of mullite seed crystals (0.1 %) | 150 ± 10 |
| Dried mullite-forming suspension | 110 ± 10 |

# EFFECT OF MECHANICAL ACTIVATION ON THE STRUCTURE OF THE Ti-Al-Nb ALLOYS OBTAINED BY THE SPS METHOD

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Due to the short-term high-temperature effect on the powder mixture, the optimum ratio of the heating and deformation modes of the material, as well as the peculiarities of the passage of an electric current through the powder mixture, the technology of electropulse plasma sintering (SPS) enables to obtain high-strength products with low values of porosity and residual mechanical stresses. It is possible to preserve the fine-grained structure of sintered material using this technology. In recent years, there has been an increase in published works on the study of titanium aluminides, including those obtained by the SPS method.

This paper presents an investigation of the influence of duration of mechanical activation on the structure of the alloy. Mechanical activation was carried out with a planetary ball mill AGO-2 at a vials rotation speed of 400 rpm. for 3 and 5 minutes. Sintering of the powder mixtures was carried out with a special Labox-1575 unit. X-ray phase analysis, raster electron microscopy, and energy-dispersive spectroscopy were used to study the resulting alloy with the construction of an element distribution map. It is established that the microstructure of the alloy sintered at a temperature of 1200 °C with preliminary mechanical activation for 3 minutes is very heterogeneous. The resulting alloys consist of phase grains of $\alpha_2$ and $Nb_2Al$ and dispersed precipitates of the O - phase, as well as of unreacted niobium and titanium particles. In comparative studies, it has been established that the microstructure of the alloy sintered at a temperature of 1200 °C with preliminary mechanical activation for 5 minutes is more uniform in comparison with the alloy mechanically activated for 3 minutes. Based on the results of X-ray phase analysis, it was found that alloys contain the same intermetallic phases ($\alpha_2$, $Nb_2Al$, O -phase) and residual Ti and Nb particles, but their ratio varies depending on the duration of mechanoactivation.

# SILVER NANOPARTICLES FORMATION IN COLLOIDAL SYSTEM AND POLYMER MATRIX

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Using UV and visible spectroscopy, atomic force microscopy, and the method of dynamic light scattering, the growth dynamics and the size distribution of Ag particles (NPs) in the polyvinyl alcohol (PVA) composition, PVA film, and aqueous sol were studied. The hypsohromic shift of the surface plasmon absorption band of Ag NPs, when changing from the PVA composition to the film, has been measured. The magnitude of the shift is 55 nm. The dynamics of Ag particles formation and the particle size have been shown to be highly dependent on the UV irradiation, ultrasonic action, and PVA concentration (Fig. 1). Thus, it has been established that UV irradiation accelerates Ag NPs formation in the presence of reducing agents and destroys the formed nanoparticles in case of the lack of the reductant. Partial Ag NPs destruction occurs under the influence of ultrasound, while, after UV irradiation, the ultrasound action leads to the reduction of Ag ions on the clusters.

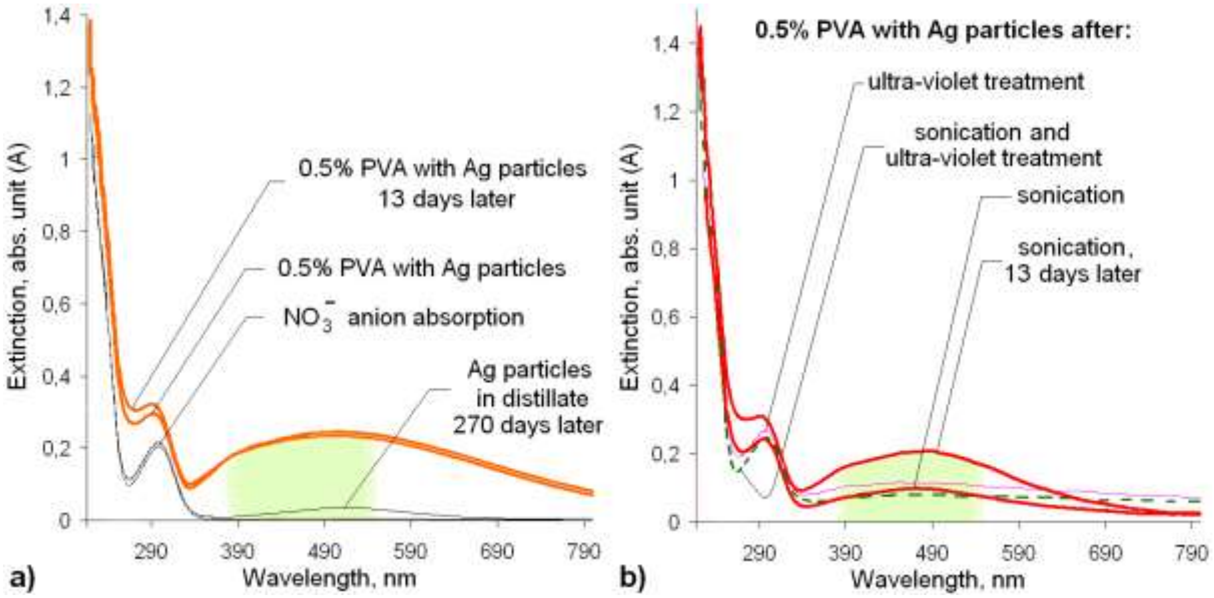

Fig. 1. Spectra of Ag sols, obtained on the basis of 0.5% PVA solution, and Ag sol in distillate
a) spectra without processing. The band of surface plasmon resonance with $\lambda_{max}$ = 490 nm, A = 0.24, the average size of Ag NPs is 80 nm.
b) spectra of sols after various effects: ultrasonic action, UV irradiation, ultrasound and UV treatment.

# MECHANICAL, CHEMICAL AND ELECTROCHEMICAL ALUMINUM SURFACE TREATMENT: MAIN RESULTS AND APPLICATIONS

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Nanoporous aluminum oxide (NAO) is the subject of intense research because of its nanoporous nature and the variety of practical applications arising from it [1-5]. The best-known application of anodizing of aluminum is that for effectively improving of the corrosion resistance of the metal [1, 2]. NAO films can be used in optical interferometric chemical sensors [3] and in micro/nanoscale lasers with indirect electrical pumping by laser diodes [4, 5]. Determination of the optimal conditions of the mechanical and electrochemical polishing, the aluminum electrochemical anodization and electrochemical and chemical metallization for each particular case is important task. This work is a logical continuation of the works [1-5]. In the present study, the optimal conditions of the mechanical, chemical and electrochemical aluminum surface treatment were determined. Using the optimal conditions, metallized NAO films were obtained. The physical and chemical properties of the obtained NAO films were studied using high resolution scanning electron microscopy and the reflective interference spectra (RIfS) in a wavelength range of 235–735 nm at different angles.

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# ANTIFRICTION MATERIALS BASED ON PTFE, OPERATED UNDER THE ARCTIC CONDITION

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This paper investigates the behavior of a polymer matrix PTFE reinforced with carbon fibers and mechanoactivated kaolin. It is shown that the use of complex fillers improves the tribotechnical properties of the polymer matrix. Complex filler improves the strength properties of polymer composites.

PTFE is engineering polymer, with unique antifriction and thermal properties. Modification of the polymer matrix by introduction of fillers results in an increase in strength and wear-resistance of PTFE. It has been shown that introduction of carbon fibers and mechanoactivated kaolin into PTFE significantly improved tribological and mechanical properties of the composite. The results are presented in the Table showing the physical-mechanical and tribotechnical characteristics of PTFE and PCM.

| Sample | $\sigma_T$, MPa | $\varepsilon_T$, % | $\sigma_c$, MPa | I, mg/h | *F* |
|---|---|---|---|---|---|
| Initial PTFE | 21 | 320 | 16 | ~120 | 0,22 |
| PTFE + 1 wt.% CFs + 1 wt.% Kl | 20 | 319 | 18 | 0,44 | 0,27 |
| PTFE + 3 wt.% CFs + 1 wt.% Kl | 20 | 294 | 21 | 0,25 | 0,28 |
| PTFE + 5 wt.% CFs + 1 wt.% Kl | 19 | 314 | 24 | 0,16 | 0,24 |
| PTFE + 8 wt.% CFs + 1 wt.% Kl | 19 | 326 | 25 | 0,17 | 0,25 |
| PTFE + 10 wt.% CFs + 1 wt.% Kl | 17 | 297 | 26 | 0,18 | 0,34 |

$\sigma_T$ – tensile strength; $\varepsilon_T$ – elongation at break; $\sigma_c$ – compressive strength (relative deformation of 10%); I – wear rate; *f* – coefficient of friction.

As it can be seen from Table, the physical-mechanical characteristics of the PCM are preserved at the level of the original PTFE. The compressive strength of PCM is increased up to 60% (at 10 wt.% CFs) and wear rate of the PCM (at 5 wt.% CFs) is 750 times larger than that of the original PTFE. Thus, the developed materials have improved properties and can be adopted in the tribology application of machines and equipment working in the North.

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# THE INTERPHASE BOUNDARIES DESIGN FOR THE SYNTHESIS OF HIGH-RESISTANT DIAMOND-HARD ALLOY MATERIALS WITH THE USE OF DIAMONDS THERMAL DIFFUSION METALLIZATION

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The results of researches in the field of fundamental and applied problems of matrix-filler interface formation for the synthesis of high-resistant diamond composites are presented. To improve of chemical and mechanical adhesion between the natural diamond particles and hard-alloy matrix a hybrid technology is offered that combines the thermal diffusion metallization of diamond and the sintering by the original scheme of self-dosed impregnation with a low-melting metal in a one-stage technological cycle. The technology eliminates the reheating of the metallized coating, in which its destruction occurs and the graphitization of the diamond is intensified. The purpose of this work is to confirm the formation of metallized coating on diamond particles and to assess of the operational properties of a diamond tool received with application of hybrid technology. By the methods of electron microscopy, X-ray diffraction analysis, and Raman spectroscopy the structural and phase organization, reaction products distribution, the structural forms of carbon (diamond, graphite) of the diamond-matrix contact zone of the diamond tool prototypes (Fig. 1*a*) were investigated. It was revealed the formation and preservation of a chromium carbide coating on diamond particles (Fig. 1*b*) during the synthesis of diamond composites using the developed hybrid technology; this ensured the monolithic and strength of the diamond-matrix transition zone. Graphitization is insignificant: free carbon was detected in small amounts in the form of micron dimension inclusions (shown by the arrows in Fig. 1*c*). The improvement of diamond retention increased the specific productivity of experienced diamond dressers by 39-45%.

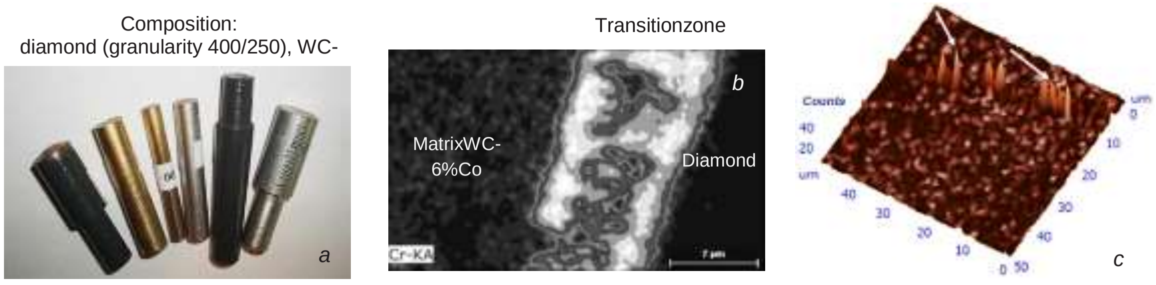

Fig. 1. Diamond tool samples (*a*), the map of the chromium distribution (*b*) and three-dimensional map of the Raman spectra of graphite formations (*c*) at the diamond-matrix transition zone in the diamond dressers.

# GEOPOLYMER BINDER BASED ON FLY ASH PREPARED USING MECHANICAL ACTIVATION

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Geopolymers are alkali-activated binders prepared from aluminosilicates of various origins. They harden at ambient conditions and are regarded as environmentally benign building materials in comparison to ordinary Portland cement due to lower $CO_2$ emissions [1]. In this work geopolymer binder has been prepared using fly ash from Apatity thermal power station (Murmansk Region). The ash contains about 65 wt % X-ray amorphous material in addition to quartz, magnetite, hematite, with minor proportions of lime, and presents considerable storage problems.

Sodium hydroxide solutions and liquid glass have been used as alkali agents in geopolymer synthesis. To increase the fly ash reactivity, mechanical activation of the ash has been carried out using AGO-2 planetary mill for up to 400 s. The particle sizes and surface areas of the as-received and mechanically activated fly ash powders have been determined. Geopolymer samples have been prepared by mixing of the as-received and mechanically activated fly ash with alkali agent and curing at 20±2 °C under relative humidity of 95±5% for up to 180 days.

Geopolymers synthesized from the as-received ash have achieved compressive strengths of only about 5 MPa. It has been shown that reduction of the particle size and accumulation of excess energy by mechanical activation of the fly ash lead to the increase of the compressive strength of the resulting alkali-activated geopolymer up to 65 MPa.

The processes occurring in the course of mechanical activation of the fly ash and during geopolymer synthesis have been studied using X-ray diffraction, FT-IR spectroscopy and complex thermal analysis.

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# DEVELOPMENT OF PCM ON THE BASIS OF PTFE AND CF USING THE TECHNOLOGY OF JOINT MECHANOACTIVATION OF COMPONENTS

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The results of development of tribological materials based on polytetrafluoroethylene (PTFE) and activated carbon fiber (CF) UVIS-AK-P trademark are presented. The influence of mixing technologies on the mechanical and tribological characteristics of polymer composites was investigated.

The aim of this paper is investigation of dependence of mechanical and tribotechnical properties of polymer composite materials (PCM) based on PTFE and UVIS-AK-P carbon fibers on regimes of activation of composite components.

The PCM was obtained by mixing the components in a high-speed blade mixer at different speeds. The concentration of the filler in the polymer matrix was 1-5%. To enhance the adhesion interaction of PCM components the technology of joint activation of components in a planetary mill at different speeds of rotation of the drums within 2 minutes was used.

Mixing of components was carried out in 2 steps: at first, some PTFE powder and required amount of CF were mechanically activated simultaneously in planetary mill at a rotation speed of the drums at 200-400 rpm, secondly, the remaining polymer powder was added in activated composition and mixing in bladed mixer was performed. For comparison, compositions were also prepared with mixing of components in 2 steps without mechanical activation.

It was established that the introduction of UVIS-AK-P up to 3 wt.% leads to increase of deformation and strength characteristics when using a simple mixing of components in a bladed mixer. Besides the addition of the filler up to 5 wt.% causes an increase of wear resistance of PCM. Activation of the components at a speed of 200-300 rpm leads to decrease of deformation and strength characteristics, improve the compressive strength of 40-60% and improving the wear resistance of PCM in 350-1250 times in comparison with initial polymer. The increase in the activation speed up to 400 rpm leads to an increase in wear resistance up to 2025 times, while the value of deformation and strength characteristics remains at the level of the original polymer or even slightly exceeds them.

# METHOD OF MANUFACTURING A PROTOTYPE OF A CORIUM BY USING STAND OF HIGH-TEMPERATURE INDUCTION HEATING

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Physical modeling, where data can be obtained to be used for solving real problems, is the most effective tool for studying the processes occurring during severe accidents in a nuclear reactor and for studying the properties of the formed alloys and compounds.

As part of above research, the Institute of Atomic Energy NNC RK (IAE) conducts experiments at the IGR research reactor and VCG-135 out-of-pile stand to study behavior of energy nuclear reactor fuel under the conditions of severe accident.

The work is focused on development of a method for manufacturing a prototype of a corium by using stand of high-temperature induction heating VCG-135

The essence of this method consists in the following sequence of necessary operations. First a tumbler with outside diameter equal to the inside diameter of the melting crucible from GMZ graphite and with height equal to the height of the crucible internal cavity is made from tantalum sheet with a thickness of 0.3 mm. Then tantalum tumbler is put into the crucible cavity, the tumbler is filled with the charge which composition repeats the composition of fuel and structural materials of the fast reactor core and the crucible is covered with a graphite cover containing a hole for sighting with a pyrometer.

The experimental assembly prepared in this way is heat isolated and put into the induction furnace of VCG-135 test bed for decontamination, first, and carbide annealing, next. The tungsten-rhenium thermocouple such as VR5/20 measuring the temperature of the outer side surface of the crucible in its middle part and IMPAC pyrometer measuring melt temperature are used for the assembly thermometry in the course of annealing.

Whereupon half-hour decontamination annealing of the heat isolated assembly is done at the temperature of 800 °C in vacuum with residual pressure of 0.1 kPa, and carburization annealing is done in helium under the pressure of 0.13 MPa in two stages: first for 3 hours at the temperature of 1300 °C, and then for 3 minutes at the temperature of ~2900 °C, that is, the temperature is a little higher than $UO_2$ dioxide fusion temperature, which is 2867 °C.

# SULFUR - PROCESSING AND APPLICATIONS

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Elemental sulfur is one of the five most widely used modern chemical products. This circumstance led to a large number of works devoted to sulfur. It seems very relevant to develop methods for using well-known valuable properties of sulfur, such as bactericidal, hydrophobic, etc. for sulfur particles. At present, great scientific expectations in this field are associated with the development of nanotechnologies, especially with the manifestation of the biological properties of sulfur nanoparticles. A distinctive characteristic of preparations based on nanotechnology is the ability to exert an effective effect on plants in very small concentrations.

In the present work, differences in the dimensions, structural and thermodynamic states of dispersed sulfur particles obtained by mechanical treatment and chemical precipitation from solutions of polysulphides are established. The conditions for separation of nanosized sulfur powder from solutions of polysulphide powders with average sizes of 20 nm have been determined, as well as further evolution of these particles into larger formations.

The use of sulfur-based products results in the suppression of all pathogens studied, and its use in the form of nanoparticles with an average size of 20 nm increases the antifungal efficacy by a factor of 10-50 compared to those obtained for microns with an average size of 70 μm. It has been established that sulfur nanoparticles have an effect on the morphological characteristics of the accelerated growth of shoots and rootlets and on the yield by an increase in the latter, as well as increased protein content in wheat grain.

# ENERGY ACCUMULATION BY DISPERSED MATERIALS

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The process of mechanical activation of a number of inorganic substances in mills of various designs is studied, the effect on the material in the constrained impact mode (planetary mills) and in the constrained impact mode (centrifugal mills, disintegrator) is compared. By thermal analysis methods it has been established that as a result of shock effects in the free-impact regime, energy storage comparable to the energy of phase transitions occurs as a result of the formation of defects in the structure of the crystal lattice. Analysis of the process of energy accumulation by dispersed particles of different chemical nature in devices with different impact characteristics has shown that the accumulation of energy in the process of machining in a centrifugal mill occurs more intensively than in a planetary mill. It is established that impact forces in a centrifugal mill lead to accumulation of excess enthalpy which manifests itself in the form of distinct exothermic peaks on DTA curves, while the thermal effects observed on DTA curves after treatment in a planetary mill are more gentle. It is established that the use of a centrifugal mill in comparison with a planetary mill is preferable in the process of mechanical activation and the production of new substances by mechanochemistry methods because of the possibility of scaling. The accumulation of excess energy in crystals with a covalent type of chemical bond and the absence of that for ionic crystals was revealed. The good agreement between the data of thermal analysis and scanning calorimetry is obtained.

# INITIATION OF THE FORMATION OF MIXTURES FROM THE ULTRA-DISPERSED α-Cu AND β-Cr PHASES BY MECHANOACTIVATION OF THE COMPOSITIONS “Cr POWDER – Cu MELT”

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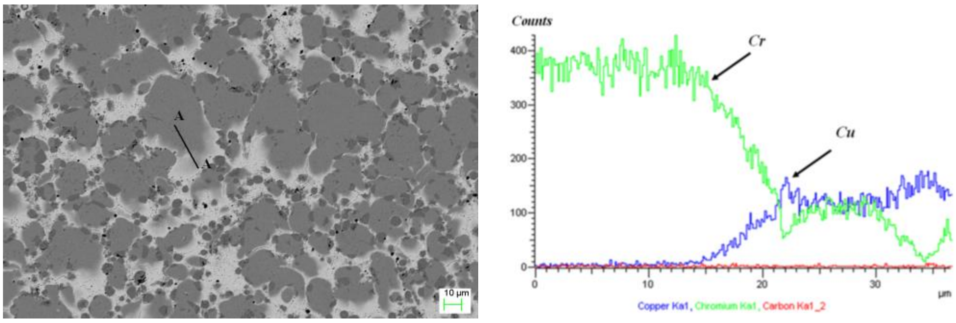
Structure formation peculiarities in the Cu-Cr composite alloys were not yet studied sufficiently. It is unknown why these composites are more arc-resistant in comparison with the Cu-W alloys when they used as electrical contacts.

The aim of this work is to study the microstructure of the Cu-Cr (1.6...90.0 at.%) alloys. The alloys mentioned were obtained using mechanical activation (by low-frequency vibration) of "Cu melt - Cr powder" compositions. Annealing temperatures of different compositions of the Cu-Cr alloys (depending on the chromium content) were chosen relative to the liquidus line. Part of the alloys samples was overheated (250 K) above liquidus temperature. Another part was exposed 200 K and 560 K below the liquidus line.

The existence of intermediate metastable structures based on ultra-dispersed mixtures of Cu and Cr was discovered (blurred regions of Cr grains in Fig. 1 (*a*)). It has been shown that the mixtures mentioned are precursors of chromium dendrites during crystallization.



*a* *b*

Fig. 1. SEM image of the Cu-Cr alloy and distribution of elements along the scan line A-A

A gradient character of elements distribution in the direction from the center of the chromium particles to the blurred interphase boundary is shown in Fig. 1 (*b*).

The formation of ultra-dispersed mixtures was activated by temperature and vibration treatment onto the Cu-Cr liquid-solid compositions.

The work was carried out within the framework of the IMET UB RAS state task No.0396-2015-0078. The equipment of Ural-M Shared Research Centre and the HitachiTM4000Plus microscope of Interlab Ltd. were used to make this study.

# STRUCTURAL STUDIES OF NANO-COMPOSITIONAL (BeO + $TiO_2$) CERAMICS

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In this paper, we studied the mechanisms of the formation of the crystal structure and the microstructure of ceramics based on beryllium oxide (BeO) and titanium dioxide in the form of a nanopowder ($TiO_2$-nano). The problems of effective mixing of nanosized powders are considered, the modes of sintering and burning of an organic binder are investigated. The ceramics of the composition (BeO + $TiO_2$) finds application in radio electronic engineering as effective absorbers of microwave radiation and in other areas of modern technology.

For the first time, the possibility of obtaining a nanocomposite ceramics of the composition BeO + $TiO_2$ was considered. A microstructural analysis of the geometric dimensions, shape and distribution of the impurity phase of the $TiO_2$ nanopowder in the BeO matrix was carried out, in comparison with the BT-30 sample manufactured using the factory technology. During the manufacture of experimental samples, factors that adversely affected the structural-phase composition of the material were identified. The developed mode of sintering allows to lower the temperature by 30 °C, which undoubtedly brings an economic effect. The structure and phase composition of nanocomposite oxide-beryllium ceramics were studied by X-ray diffraction, and crystal-geometric schemes of oriented intergrowth of $TiO_2$ and BeO crystallites, leading to the formation of an intermediate layer with a perovskite structure, were determined.

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