INCOME 2011

Programme and the Book of Abstracts

VII International Conference on

MECHANOCHEMISTRY AND MECHANICAL ALLOYING

Herceg Novi, Montenegro, August 31 – September 3, 2011

Organised by

MATERIALS RESEARCH SOCIETY OF SERBIA

under the auspices of

INTERNATIONAL MECHANOCHEMISTRY ASSOCIATION

VII INTERNATIONAL CONFERENCE ON MECHANOCHEMISTRY AND MECHANICAL ALLOYING

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http://www.mrs-serbia.org.rs/income2011/income2011.html

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International Mechanochemistry Association

Title: VII International Conference on Mechanochemistry and
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Publisher: Materials Research Society of Serbia
Knez Mihailova 35/IV; 11000 Belgrade, Serbia
Phone: +381 11 2185-437; Fax: + 381 11 2185-263
http://www.mrs-serbia.org.rs

Editor: Prof. Dr. Dragan P. Uskoković

Technical editor: Aleksandra Stojičić

Cover page: Aleksandra Stojičić and Milica Ševkušić

Acknowledgment:

NT-MDT
INTEGRATED SOLUTIONS FOR NANOTECHNOLOGY

Printed in: Biro Konto
Sutorina bb, Igalo – Herceg Novi, Montenegro
Phones: +382-31-670123, 670025, E-mail: bkonto@t-com.me
Circulation: 200 copies. The end of printing: August 2011

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WELCOME SPEECH BY THE PRESIDENT OF THE INTERNATIONAL MECHANOCHEMISTRY ASSOCIATION

Dear Participants,

It is my great pleasure to welcome you to INCOME 2011, which is the seventh event under the same title, started 1993 in Košice, after a long incubation period.

INCOME2011 is held immediately before YUCOMAT 2011, organized by the Materials Research Society of Serbia, headed by Prof. Dragan Uskokovic. I would like to sincerely appreciate their time and efforts paid to link these two conferences together.

Scientific and technological interests associated with mechanochemistry are ever expanding. Increasing number of people in the organic or biological communities, for instance, are now trying to apply some of the phenomena associated with the interplay between the chemical bonding and mechanical stressing, elucidated preferentially in the inorganic or metallic worlds.

INCOME will serve to make the concepts of mechanochemistry more established. In this context, I really hope lively discussions. This will trigger further interdisciplinary and international cooperation, leading to better understanding of the guiding principles and fruitful applications to diversity of the developing technologies. Please enjoy your stay at the really nice resort area of Herceg Novi.

Mamoru Senna

GENERAL INFORMATION

BACKGROUND

Since the classical papers by M. Carey Lea on mechanical activation of solids over hundred years back (1893–94), mechanochemistry and mechanical activation have moved a long way and evolved as a frontier area of research and applications, during the last two to three decades. Notable developments have taken place in terms of scientific understanding and applications in diverse fields, encompassing all facets of metallurgy including metal extraction, alloying, composites; traditional and advanced ceramics processing; paints, pigments and dyes; catalysis, pharmaceuticals, agriculture, utilization of wastes, energy and environment, and many more. Simultaneous developments have taken place in terms of characterization techniques of activated solids; quantification and control of activation processes; and mechanical activation devices for specific needs, etc.

The INCOME series of conferences initiated by International Mechanochemistry Association [an associate member of International Union of Pure and Applied Chemists (IUPAC)] has served as a common platform to bring together all stakeholders from academia, Research and Development organisations, and industry to foster the growth of the discipline. The first international conference on ‘Mechanochemistry and Mechanical Alloying’ (INCOME 1993) was held in Košice (Slovakia) in 1993. This was followed by INCOME 1997 in Novosibirsk (Russia), INCOME 2000 in Prague (Czech Republic); INCOME 2003, in Braunschweig (Germany), INCOME 2006 again in Novosibirsk, and INCOME 2008 in Jamshedpur (India).

The developments in the field of mechanochemistry are unfolding at a rapid rate in terms of basic science, range of applications, and their impact. While significant advances are taking place in each of the application areas, e.g. smart mechanochemistry, pharmaceuticals, etc., and call for periodic review, the need for cross fertilization of concepts and ideas is increasingly becoming apparent. The next conference of the series, INCOME 2011, will be held in Herceg Novi, Montenegro, from August 31 – September 3, 2011. The conference aims to provide a forum for presentation of new results, identification of current research & development trends and future directions, and promote interactions among various stakeholders dealing with various aspects of the discipline. It is also proposed to organize an exhibition on the sideline of the conference to provide an opportunity to related institutes/companies for the display of their products.

SCOPE OF THE CONFERENCE

The scientific program will consist of invited lectures, oral, and poster communications. The conference will touch upon all facets of mechanochemistry, including

- Synthesis and processing in solid-state science and technology
  Mechanosynthesis, Mechanical alloying, Mechanical activation, High-energy milling, Severe plastic deformation of materials (SPD), Role of environment (e.g. water, gases), Reaction milling, and Mechanochemical processing under less intensive stressing (soft mechanochemistry, smart mechanochemistry, etc.), Mechanochemistry of macromolecules.
- Structural characterization
  Mechanically induced structural changes in activated solids, Role of defects (point defects, dislocations, clusters, precipitates, grain boundaries), Surfaces and interfaces in activated solids.

- Thermodynamics and modeling
  Fundamentals and models of mechanically stimulated processes, Computer simulations.
- Kinetics of solid state processes
  Evolution toward equilibrium, Phase transitions, Crystal growth, Transport processes.
- Properties
  e.g., chemical, electrochemical, electrical, magnetic, electronic, optical, tribological, thermal, and mechanical.
- New materials/processes
  Nanomaterials, nano-composites, quasi-crystalline phases/materials, molecular design, coatings, self propagating high temperature synthesis
- Applications (including new commercial processes)
  Mechanical alloying, Metal extraction, Leaching of minerals and ores, Ceramics processing, Catalysis, Paints, pigments and dyes, Cement processing, Mechano-organo/organometallic synthesis, Pharmaceutical, Agriculture, Waste utilisation, Ecologically safe technologies, etc.
- New equipment and procedures
  Milling equipment based on improved milling dynamics, Large size activation devices, Preparation, characterization and handling of active powders

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GENERAL PROGRAM

Day 1

9	0	Opening	
9	15		
9	30	Plenary 1	Sepelak
9	45		
10	0		
10	15	Keynote 1	Rojac
10	30		
10	45	Break (15 min)	
11	0	Keynote 2	Fabian
11	15		
11	30	Keynote 3	Zhang
11	45		
12	0	Keynote 4	Heitjans
12	15		
12	30	Lunch (90 min)	
13	0		
13	30		
14	0	1A 120 min	1B 120 min
14	15	Oral 1-6	Oral 7-12
14	30		
14	45		
15	0		
15	15		
15	30		
15	45		
16	0	Break (15min)	
16	15	1C 120 min	1D 100 min
16	30	Oral 13-18	Oral 19-23
16	45		
17	0		
17	15		
17	30		
17	45		

Day 2

9	0	Plenary 2	Lyakhov
9	15		
9	30		
9	45	Keynote 4	Naumov
10	0		
10	15	Keynote 5	Balaz
10	30		
10	45	Break (15 min)	
11	0	2A 120 min	2B 120 min
11	15	Oral 24-29	Oral 30-35
11	30		
11	45		
12	0		
12	15		
12	30		
12	45		
13	0	Lunch (60 min)	
13	30		
14	0	(30min cushion)	
14	30	Excursion	
14	45		
15	0		
15	15		
15	30		
15	45		
16	0		
16	15		
16	30		
16	45		
17	0		
17	15		
17	30		
17	45		

18	0			18	0	
18	15	(30min cushion)		18	15	
18	30	Cocktail		18	30	
18	45			19	0	
19	0			19	15	(30min cushion)
19	15			19	30	Poster 1 (120 min)
19	30			20	0	
19	45			20	30	
20	0			21	0	
21	0			21	30	

Day 3				**Day 4**			
9	0	Plenary 3	Mukhopadhyay	9	0	Plenary 4	Saito
9	15			9	15		
9	30			9	30		
9	45	Keynote 6	Olezak	9	45	Keynote 12	Jones
10	0			10	0		
10	15	Keynote 7	Tacaks	10	15	Keynote 13	Bolm
10	30			10	30		
10	45	Break (15 min)		10	45	Break (15 min)	
11	0	3A 60 min	3B 60 min	11	0	4A 60 min	4B 60 min
11	15	Oral 36-38	Oral 39-41	11	15	Oral 59-61	Oral 62-64
11	30			11	30		
11	45			11	45		
12	0	Lunch (90 min)		12	0	Closing	
13	0			12	15	End of the Symposium	
13	15			12	30		
13	30	Keynote 8	Begin-Colin				
13	45						
14	0	Keynote 9	Calka				
14	15						
14	30	Break (15min)					
14	45	3C 100 min	3D 100 min				
15	0	Oral 42-46	Oral 47-50				
15	15						

15	30		
15	45		
16	0		
16	15		
16	25	Break (20min)	
16	45	Keynote 10	Schmidt
17	0		
17	15	Keynote 11	Yermakov
17	30		
17	45	3E 80 min	3F 80 min
18	0	Oral 51-54	Oral 55-58
18	15		
18	30		
19	0		
19	15	(30min cushion)	
19	30	Poster 2 (120 min)	
20	0		
20	30		
21	0		
21	30		

TENTATIVE PROGRAM

Code	Pres Style	OrlNo	Title
A153	Plenary		MECHANOCHEMISTRY OF COMPLEX OXIDES
A048	Keynote		MECHANOCHEMICAL SYNTHESIS OF ALKALINE NIOBATES AND TANTALATES: UNDERSTANDING REACTION MECHANISMS
A112	Keynote		CHARACTERIZATION OF COMPLEX OXIDES PREPARED BY BALL MILLING
A158	Keynote		MECHANOCHEMICAL LEACHING OF SPHALERITE IN AN ALKALINE SOLUTION
A163	Keynote		NMR STUDIES IN MECHANOCHEMISTRY
A010	Oral	Mater01	SYNTHESIS OF FINE $Ni_{75}Mg_{16.66}Y_{8.34}$ (at %) POWDER FOR USING AS A CATALYST BY SOLID REACTION AND MECHANICAL MILLING
A018	Oral	Mater02	POSSIBILITIES OF EXCHANGE MECHANOCHEMICAL REACTIONS FOR PREPARATION OF DISPERSE CERAMIC MATERIALS
A020	Oral	Mater03	CORROSION STUDY AND SURFACE CHARACTERIZATION OF SOME PROCESS VARIABLES ZINC PLATED MILD STEEL IN HCL SOLUTION
A021	Oral	Mater04	ANTIMICROBIAL AND ANTIOXIDANT ACTIVITIES AND PHYTOCHEMICAL SCREENING OF THE PLANT *KITAIBELIA VITIFOLIA*
A022	Oral	Mater05	DEFORMATION OF GRAPHENE AND ITS CHEMICALLY MODIFIED ANALOGUES AS MECHANOCHEMICAL REACTION
A030	Oral	Mater06	CERAMIC SSZ/ZIRCONIA NANOCOMPOSITE WITH HIGH CONDUCTIVITY
A040	Oral	Mater08	MECHANOCHEMICAL SYNTHESIS OF ULTRAFINE LITHIUM GAMMA-MONOALUMINATE
A050	Oral	Mater09	LOW-TEMPERATURE SYNTHESIS OF ALUMINUM NITRIDE
A064	Oral	Mater10	NEW MECHANOCHEMICAL AND MICROWAVE METHODS FOR SYNTHESIS OF PLATINUM GROUP METAL BETA-DIKETONATES AS MOCVD PRECURSORS

A069	Oral	Mater11	**MULTISCALE DESIGN OF CoAlO/CoAl CERMET PREPARED FROM Co-Al ALLOYED PRECURSOR**
A073	Oral	Mater12	**MECHANOCHEMICAL SYNTHESIS OF NANOPHASE COMPOSITES IN $La_{1-x}Sr_xFeO_{3-y}$ PEROVSKITES: FORMATION OF $LaSrFeO_4$ SURFACE RICH COMPOSITES**
A078	Oral	Mater13	**Cu/ZrO_2 COMPOSITES PREPARED BY SELF-PROPAGATING HIGH-TEMPERATURE PROCESSING OF THE MECHANICALLY PRE-ACTIVATED CuO/Cu/Zr SYSTEM**
A079	Oral	Mater14	**THE PREPARATION OF MECHANOCOMPOSITES W-Me-ORGANIC SUBSTANCE AND INVESTIGATION OF THE INFLUENCE OF TYPE OF ORGANIC PLASTICIZER ON THE COMPRESSIBILITY OF THE OBTAINED MECHANOCOMPOSITES**
A080	Oral	Mater15	**MECHANICAL BEHAVIOR OF MECHANICALLY ACTIVATED CARBON-QUASICRYSTAL COMPOSITE**
A084	Oral	Mater16	**CRYSTALLINE/MAGNETIC STRUCTURE OF $LA_{0.54}PR_{0.11}PB_{0.35-X}SR_XMNO_3$ OBTAINED BY HIGH-ENERGY MILLING**
A085	Oral	Mater17	**INFLUENCE OF HIGH-ENERGY MILLING ON THE STRUCTURE AND TRANSPORT PROPERTIES OF $LA_{0.54}HO_{0.11}CA_{0.35}MN_{1-X}CR_XO_3$**
A096	Oral	Mater18	**THE HIGH TEMPERATURE FINE GRINDING OF POLYMERS UNDER ACTION OF INTENSE SHEAR STRESS AS A MECHANOCHEMICAL AVALANCHE-LIKE CRACKING PROCESS OF POLYMERS**
A113	Oral	Mater19	**DEVELOPPING OF MAGNESIUM AND MAGNESIUM-SCANDIUM SYSTEMS WITH OPTIMIZED HYDROGEN SORPTION FOR VLi BATTERIES APPLICATION**
A119	Oral	Mater20	**CHARACTERIZATION OF MECHANOSYNTHESIZED NON-EQUILIBRIUM FLUORIDES BY HIGH-RESOLUTION SOLID STATE NMR – CORRELATION OF STRUCTURAL FEATURES WITH IONIC CONDUCTIVITY**
A127	Oral	Mater21	**SYNTHESIS AND REACTION SINTERING OF MECHANOCHEMICALLY PROCESSED YAG:Ce PRECURSOR**
A132	Oral	Mater22	**CATALYTIC ACTIVITY OF $La_{0.4}Sr_{0.6}FeO_3$ PEROVSKITES PREPARED VIA MECHANOCHEMICAL ROUTE IN N_2O DECOMPOSITION PROCESS VERSUS Sr-**

			CONTAINING PRECURSOR
A151	Oral	Mater23	**MECHANOCHEMICAL SURFACE TREATMENT**
A052	Oral	Proc	**AN INVESTIGATION ON MECHANOCHEMICAL ACTIVATION OF SOLIDS AND ITS APPLICATION TO MATERIAL PROCESSING**
A103	Poster	P_Mater1	**'HEDVALL EFFECT' IN CRYOGRINDING OF MOLECULAR CRYSTALS. A CASE STUDY OF A POLYMORPHIC TRANSITION IN CHLORPROPAMIDE**
A105	Poster	P_Mater2	**MONITORING MECHANICAL PROPERTIES OF INDIVIDUAL HYDROGEN BONDS: SINGLE-CRYSTAL X-RAY DIFFRACTION AND POLARIZED RAMAN SPECTROSCOPY IN SITU**
A025	Poster	P_Mater3	**THE INFLUENCE OF MAGNETIC ORDERING ON THE PHYSICAL PROPERTIES OF $CuFeS_2$**
A026	Poster	P_Mater4	**THE MACRO- AND CRYSTALLOGRAPHIC STRUCTURE OF Li-Ti-Zn-FERRITES PREPARED WITH BALL-MILLING PROCEDURE**
A028	Poster	P_Mater5	**THE INFLUENCE OF D-GUN SPRAYING CONDITIONS ON THE STRENGTHENING AND DEFORMATION OF THE Fe-Al TYPE INTERMETALLIC COATINGS**
A029	Poster	P_Mater6	**THERMAL STABILITY OF THE Fe-Al TYPE INTERMETALLICS COATINGS OBTAINED BY D-GUN SPRAYING**
A035	Poster	P_Mater10	**DEVELOPMENT OF CATHODES ($La_{1-x}Sr_xMnO_{3\pm\delta}$) FOR SOLID OXIDE FUEL CELLS BY MECHANOSYNTHESIS**
A039	Poster	P_Mater11	**DEVELOPMENT OF $Ti_XTa_{1-x}C_yN_{1-Y}$-BASED CERMETS VIA A MECHANICALLY INDUCED SELF-SUSTAINING REACTION**
A045	Poster	P_Mater12	**MECHANOCHEMICAL SYNTHESIS OF THE LITHIUM-ALUMINIUM ANIONIC CLAYS**
A059	Poster	P_Mater13	**TOPOLOGICAL MODELS FOR SELF-ADAPTIVE NETWORK CLUSTERS IN CHALCOGENIDE GLASSY-LIKE ALLOYS**
A060	Poster	P_Mater14	**ROLE OF FREE-VOLUME COORDINATION DEFECTS IN EQUILIBRIUM-RELAXATION PROCESSES IN MIXED ARSENIC-ANTIMONY-SULPHUR GLASSY ALLOYS**
A061	Poster	P_Mater15	**INFLUENCE OF HIGH- ENERGY BALL MILLING OF TUNGSTEN OXIDE WO_3 PRECURSOR ON THE TUNGSTEN NITRIDE W_2N PERFORMANCE IN SUPERCAPACITORS**

A070	Poster	P_Mater16	**THE MICROSTRUCTURE AND PROPERTIES OF ZnO ACTIVATED BY BALL MILLING**
A071	Poster	P_Mater17	**PREPARATION OF TiO_2/MoO_3 MIXED OXIDE POWDERS BY BALL MILLING**
A072	Poster	P_Mater18	**INFLUENCE OF SUBSTITUTION OF TANTALUM FOR HAFNIUM ON THE ELECTRONIC STRUCTURE OF CUBIC $Hf_xTa_{1-x}C_y$ CARBIDES: *AB INITIO* BAND-STRUCTURE CALCULATIONS AND X-RAY SPECTROSCOPY STUDIES**
A074	Poster	P_Mater19	**HYDRIDING PROPERTIES OF MAGNESIUM-BASED NANOCOMPOSITES**
A075	Poster	P_Mater20	**MECHANICAL OSCILLATIONS AND THERMODYNAMICS OF EXTRATHIN CRYSTALLINE FILMS**
A076	Poster	P_Mater21	**MONTE CARLO STUDY OF PHONON SUBSYSTEM IN ULTRATHIN CRYSTALLINE SAMPLES**
A081	Poster	P_Mater22	**INFLUENCE OF MECHANICAL ACTIVATION ON SPHENE CERAMIC SYNTHESIS**
A082	Poster	P_Mater23	**AN INFLUENCE OF TEMPERATURE ON THE PROCESS OF CHEMICAL INTERACTION OF THE MEHANOSYNTHESIZED COPPER COMPOUNDS WITH LIQUID GALLIUM AND ON THE OBTAINED PRODUCT CHARACTERISTICS**
A083	Poster	P_Mater24	**THERMOMECHANICAL CHARACTERISTICS OF ARSENIC-SULPHIDE GLASS DOPED WITH BISMUTH**
A098	Poster	P_Mater25	**MECHANOCHEMICAL PREPARATION AND SOLID-STATE CHARACTERIZATION OF COMPOSITES OF BETULIN AND ITS ETHERS**
A106	Poster	P_Mater26	**SHS OF SYSTEM WITH ACTIVATED SILUMIN**
A110	Poster	P_Mater27	**OPTICAL PROPERTIES OF NICKEL MANGANITE CERAMICS OBTAINED FROM MECHANICALLY ACTIVATED POWDERS**
A120	Poster	P_Mater28	**MECHANICAL MILLING OF MAGNESIUM BASED COMPOSITES FOR HYDROGEN STORAGE**
A121	Poster	P_Mater29	**PROPERTIES OF MECHANOCHEMICALLY SYNTHESIZED Bi_2S_3 NANOPARTICLES**
A122	Poster	P_Mater30	**KINETICS OF MECHANOCHEMICAL REDUCTION OF SPHALERITE WITH MAGNESIUM BY HIGH-ENERGY MILLING**
A125	Poster	P_Mater31	**MECHANICAL PROPERTIES OF WOOD FLOUR FILLED NR/CSM RUBBER COMPOSITES**

A126	Poster	P_Mater32	**MECHANOCHEMICAL PRECURSOR PREPARATION FOR NICKEL MOLIBDATE SYNTHESIS IN THE SYNCHROTRON RADIATION ANOMALOUS DIFFRACTION HIGH TEMPERATURE IN SITU CHAMBER**
A128	Poster	P_Mater33	**INFLUECE OF PROCESSING METHOD ON DIELECTRIC PROPERTIES OF $BaBi_4Ti_4O_{15}$ CERAMICS**
A129	Poster	P_Mater34	**EFFECT OF SOLIDIFICATION RATE AND HEAT TREATING ON THE MICROSTRUCTURE AND TENSILE BEHAVIOR OF AN Al-Cu-Mg ALLOY**
A131	Poster	P_Mater35	**MECHANOCHEMICAL SYNTHESIS OF MULTIFERROIC YTTRIUM MANGANITE**
A134	Poster	P_Mater36	**INFLUENCE OF MECHANOCHEMICAL ACTIVATION ON SINTERING OF CORDIERITE CERAMICS WITH THE PRESENCE OF Bi_2O_3 AS A FUNCTIONAL ADDITIVE**
A135	Poster	P_Mater37	**RAMAN SPECTROSCOPY STUDY OF $NiFe_2O_4$ POWDERS OBTAINED BY SOFT MEHANOCHEMICAL SYNTHESIS**
A150	Poster	P_Mater38	**THE MORPHOLOGY, STRUCTURE AND LUMINESCENT PROPERTIES OF Gd_2O_3:Eu SYNTHESIZED BY AEROSOL ROUTE AND HIGH ENERGY BALL MILLING**
A161	Plenary		**MECHANOCHEMISTRY IN MATERIALS PREPARATION**
A003	Keynote		**NEW INSIGHTS INTO THE MECHANISM OF PHOTOINDUCED, THERMALLY INDUCED AND MECHANICALLY INDUCED EFFECTS IN MOLECULAR CRYSTALS**
A006	Keynote		**ARSENIC MECHANOCHEMISTRY: FROM MINERALS ENGINEERING TO CANCER TREATMENT**
A005	Oral	Proc25	**MECHANOCHEMICAL SYNTHESIS OF CARBON NANOMATERIALS BY A HIGH-SPEED BALL-MILLING PROCESS**
A012	Oral	Proc26	**ENERGY TRANSFORMATIONS IN A CENTRIFUGAL AND PLANETARY GRINDING MILLS**
A043	Oral	Proc29	**MECHANOCHEMICAL SYNTHESIS OF NANOCRYSTALLINE SOLID FLUORIDES**
A066	Oral	Proc30	**DEVELOPMENT OF ENERGY APPROACH FOR ANALYSIS OF MECHNOCHEMICAL PROCESSES DYNAMICS**

A145	Oral	Proc34	**STEPS OF FINE GRINDING OF RICE HUSK AND CEREAL STRAW**
A001	Oral	Proc24	**PIV MEASUREMENT OF THE SHELL SIDE FLOW CHARACTERISTICS OF SHELL-AND-TUBE LNG VAPORIZER**
A013	Oral	Proc27	**EFFECT OF NANO-STRUCTURED STATES FORMATION IN ION-IRRADIATED Pt**
A037	Oral	Proc28	**SYNTHESIS OF ZnSe BY A MECHANICALLY-INDUCED SELF-SUSTAINING REACTION: A CASE STUDY FOR THE IGNITION TIME DEPENDENCE ON MILLING PARAMETERS**
A118	Oral	Proc31	**THE USING OF SYNCHROTRON RADIATION FOR MECHANOCHEMICAL PROCESS INVESTIGATION: MODEL AND REAL EXPERIMENTS**
A143	Oral	Proc33	**CHITOSAN/POLYESTER MATERIALS OBTAINED IN SOLID STATE**
A148	Oral	Proc35	**MECHANOCHEMICAL DESTRUCTION OF WATER-SOLUBLE POLYSACCHARIDES**
A101	Poster	P_Proc39	**FOLLOWING THE PRODUCTS OF MECHANOCHEMICAL SYNTHESIS STEP AFTER STEP**
A054	Poster	P_Proc40	**SOLID-LIQUID MECHANICAL SYNTHESIS OF NANOCOMPOSITES BASED ON HYDRIDE/CARBIDE-FORMING METALS**
A056	Poster	P_Proc41	**INITIAL STAGE AND MECHANISMS OF MECHANICAL SYNTHESIS IN EXOTERMIC SYSTEM Ti-C**
A090	Poster	P_Proc42	**MECHANOCHEMICAL SYNTHESIS OF MgH_2-TiB_2 COMPOSITES FOR HYDROGEN STORAGE**
A093	Poster	P_Proc43	**EFFECT OF THIRD ELEMENTS ON THE PARTICLE SIZE OF DISPERSOIDS IN MECHANICALLY ALLOYED Ni-Cr-Y_2O_3 ALLOYS**
A107	Poster	P_Proc44	**PROPOSAL OF A NEW MECHANOCHEMICAL PHASE DIAGRAM FOR THE BINARY SYSTEM Cu-Zn**
A114	Poster	P_Proc45	**MULTIFERROIC PEROWSKITE MATERIALS OBTAINED BY REACTIVE GRINDING**
A002	Poster	P_Proc46	**PROCESSING OF EGGSHELL BIOMATERIAL BY HIGH ENERGY MILLING AND EDAMM TECHNIQUES**
A027	Poster	P_Proc47	**MECHANOCHEMICAL PRODUCTION OF THE PREPARATIONS MADE OF RICE HUSK**

A036	Poster	P_Proc48	**MECHANOCHEMICAL AND CATALYTIC HYDRODECHLORIN OF POLYCHLORINATED AROMATIC COMPOUNDS**
A047	Poster	P_Proc49	**THE ACTIVATION BY LIQUID – PHASE DISPERSION**
A130	Poster	P_Proc50	**THERMODYNAMICS OF REACTIVE DYE ADSORPTION FROM AQUEOUS SOLUTION ON THE THERMAL POWER STATION ASHES**
A139	Poster	P_Proc51	**CATALYST COMPONENT INTERACTIONS IN ZINC ALUMINATE SPINEL CATALYST**
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A059	**TOPOLOGICAL MODELS FOR SELF-ADAPTIVE NETWORK CLUSTERS IN CHALCOGENIDE GLASSY-LIKE ALLOYS** O. Shpotyuk[1,2], V. Boyko[1], M. Hyla[2], L. Shpotyuk[1], J. Filipecki[2] [1]*Lviv Scientific Research Institute of Materials of SRC "Carat", Lviv, Ukraine* [2]*Institute of Physics of Jan Dlugosz University, Czestochowa, Poland*
A060	**ROLE OF FREE-VOLUME COORDINATION DEFECTS IN EQUILIBRIUM-RELAXATION PROCESSES IN MIXED ARSENIC-ANTIMONY-SULPHUR GLASSY ALLOYS** M. Vakiv[1], Ya. Shpotyuk[1-3], J. Filipecki[3] [1]*Lviv Scientific Research Institute of Materials of SRC "Carat", Lviv, Ukraine,* [2]*Ivan Franko National University of Lviv, Lviv, Ukraine,* [3]*Institute of Physics of Jan Dlugosz University, Czestochowa, Poland*
A061	**INFLUENCE OF HIGH- ENERGY BALL MILLING OF TUNGSTEN OXIDE WO_3 PRECURSOR ON THE TUNGSTEN NITRIDE W_2N PERFORMANCE IN SUPERCAPACITORS** O. Kartachova, A.M. Glushenkov, Y. Chen *Institute for Technology Research and Innovation, Deakin University, Waurn Ponds, VIC, Australia*
A062	**THE EFFECT OF TEMPERATURE DURING MECHANICAL TREATMENT ON CONVERSION OF ORGANIC PART OF BROWN COAL** V.G. Surkov, A.K. Golovko, G.S. Pevneva *Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia*
A063	**THE EFFECT OF MECHANICAL TREATMENT INTENSITY ON COMPONENT COMPOSITION OF HIGHLY PARAFFINIC CRUDE** V.G. Surkov, M.V. Mozhayskaya, A.K. Golovko *Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia*
A064	**NEW MECHANOCHEMICAL AND MICROWAVE METHODS FOR SYNTHESIS OF PLATINUM GROUP METAL BETA-DIKETONATES AS MOCVD PRECURSORS** B.R. Chimitov, K.V. Zherikova, A.N. Mikheev, N.B. Morozova *Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia*
A065	**Fe-BASED AMORPHOUS AND NANOCRYSTALLINE ALLOYS PROCESSED BY MECHANICAL ALLOYING** D. Oleszak *Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland*
A066	**DEVELOPMENT OF ENERGY APPROACH FOR ANALYSIS OF MECHNOCHEMICAL PROCESSES DYNAMICS** P.Yu. Butyagin, A.N. Streletskii *Institute of Chemical Physics RAS, Moscow, Russia*

A069	**MULTISCALE DESIGN OF CoAlO/CoAl CERMET PREPARED FROM Co-Al ALLOYED PRECURSOR** A.S. Andreev, A.N. Salanov, S.V. Cherepanova, V.I. Zaikovskii, S.F. Tikhov, V.V. Usoltsev, O.B. Lapina, V.A. Sadykov *Boreskov Institute of Catalysis, Novosibirsk, Russia*
A070	**THE MICROSTRUCTURE AND PROPERTIES OF ZnO ACTIVATED BY BALL MILING** Y. Dimitriev[1], M. Gancheva [2], R. Iordanova[2] *[1]University of Chemical Technology and Metallurgy, Sofia, Bulgaria, [2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*
A071	**PREPARATION OF TiO_2/MoO_3 MIXED OXIDE POWDERS BY BALL MILLING** R. Iordanova[1], M. Gancheva [1], Y. Dimitriev[2] *[1]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria, [2]University of Chemical Technology and Metallurgy, Sofia, Bulgaria*
A072	**INFLUENCE OF SUBSTITUTION OF TANTALUM FOR HAFNIUM ON THE ELECTRONIC STRUCTURE OF CUBIC $Hf_xTa_{1-x}C_y$ CARBIDES: *AB INITIO* BAND-STRUCTURE CALCULATIONS AND X-RAY SPECTROSCOPY STUDIES** A.A. Lavrentyev,[1] B.V. Gabrelian,[1] V.B. Vorzhev,[1] I.Ya. Nikiforov,[1] A.V. Izvekov,[2] O.Yu. Khyzhun[2] *[1]Department of Physics, Don State Technical University, Rostov-on-Don, Russian Federation, [2]Frantsevych Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kyiv, Ukraine*
A073	**MECHANOCHEMICAL SYNTHESIS OF NANOPHASE COMPOSITES IN $La_{1-x}Sr_xFeO_{3-y}$ PEROVSKITES: FORMATION OF $LaSrFeO_4$ SURFACE RICH COMPOSITES** I.S. Yakovleva, A.N. Nadeev, L.A. Isupova *Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*
A074	**HYDRIDING PROPERTIES OF MAGNESIUM-BASED NANOCOMPOSITES** I. Konstanchuk[1], K. Gerasimov[1], A. Demkin[1], J.-L. Bobet[2] *[1]Institute of Solid State and Mechanochemistry of Siberian Branch of RAS, Novosibirsk, Russia, [2]Institut de Chimie de la Matière Condensée de Bordeaux ICMCB-CNRS, Université Bordeaux 1, Bordeaux, France*
A075	**MECHANICAL OSCILLATIONS AND THERMODYNAMICS OF EXTRATHIN CRYSTALLINE FILMS** J.P. Šetrajčić [1,*], V.M. Zorić [1], I.J. Šetrajčić [1], N.V. Delić [1], S. Armaković [1], D.Lj. Mirjanić [2,*], A.J. Šetrajčić-Tomić [3], S.K. Jaćimovski [4], D. Rodić [1], S.S. Pelemiš [5] *[1]University of Novi Sad, Faculty of Sciences, Department of Physics, Vojvodina – Serbia, [2]University of Banja Luka, Medical Faculty, Republic of Srpska – B&H, [3]University of Novi Sad, Medical Faculty, Department of Pharmacy, Vojvodina – Serbia, [4]Academy of Criminalistic and Police Studies, Zemun – Belgrade, Serbia, [5]University of East Sarajevo, Faculty of Technology, Zvornik, Republic of Srpska – B&H, *Academy of Sciences and Arts of the Republic of Srpska – B&H*

A076	**MONTE CARLO STUDY OF PHONON SUBSYSTEM IN ULTRATHIN CRYSTALLINE SAMPLES** S. Armaković[1], I.J. Šetrajčić[1], D. Ćulibrk[2], J.P. Šetrajčić[1,*], B. Markoski[3], Z. Ivanković[3], B. Škipina[4], D.I. Ilić[2], S.M. Vučenović[5] *[1]University of Novi Sad, Faculty of Sciences, Department of Physics, Vojvodina – Serbia, [2]University of Novi Sad, Faculty of Technical Sciences, Vojvodina – Serbia, [3]University of Novi Sad, Technical Faculty, Zrenjanin, Vojvodina – Serbia, [4]University of Banja Luka, Faculty of Technology, Republic of Srpska – B&H, [5]University of Banja Luka, Faculty of Sciences – Physics, Republic of Srpska – B&H, *Academy of Sciences and Arts of the Republic of Srpska – B&H*
A077	**MECHANOCOMPOSITES WITH ACTIVE METALS FOR THE TRADITIONAL METHODS OF OXIDES REDUCTION** N. Lyakhov, T. Grigoreva *Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia*
A078	**Cu/ZrO_2 COMPOSITES PREPARED BY SELF-PROPAGATING HIGH-TEMPERATURE PROCESSING OF THE MECHANICALLY PRE-ACTIVATED CuO/Cu/Zr SYSTEM** T. Grigoreva[1], N. Lyakhov[1], V. Šepelák[2], I. Vorsina[1], A. Barinova[1], A. Ilyushchenko[3], A. Letsko[3], T. Talako[3] *[1]Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia, [2]Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany, [3]Powder Metallurgy Institute, Minsk, Belarus*
A079	**THE PREPARATION OF MECHANOCOMPOSITES W-Me-ORGANIC SUBSTANCE AND INVESTIGATION OF THE INFLUENCE OF TYPE OF ORGANIC PLASTICIZER ON THE COMPRESSIBILITY OF THE OBTAINED MECHANOCOMPOSITES** T. Grigoreva[1], L. Dyachkova[2], A. Barinova[1], S. Tsibulya[3], N. Lyakhov[1] *[1]Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia, [2]Powder Metallurgy Institute, Minsk, Belarus, [3]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*
A080	**MECHANICAL BEHAVIOR OF MECHANICALLY ACTIVATED CARBON-QUASICRYSTAL COMPOSITE** T.P. Yadav[1], D. Singh[1], N.K. Mukhopadhyay[2], O.N. Srivastava[1] *[1]Department of Physics, Banaras Hindu University, Varanasi, India* *[2]Department of Metallurgical Engineering, Institute of Technology, Banaras Hindu University, Varanasi, India*
A081	**INFLUENCE OF MECHANICAL ACTIVATION ON SPHENE CERAMIC SYNTHESIS** J. Pantić[1], M. Prekajski[1], B. Matović[1], A. Radosavljević Mihajlović[1], A. Kremenović[2], M. Logar[2] *[1]Department of Material Science, Institute of Nuclear Sciences Vinča, Belgrade, Serbia* *[2]Faculty of Mining and Geology, University of Belgrade, Belgrade, Serbia*

A082	**AN INFLUENCE OF TEMPERATURE ON THE PROCESS OF CHEMICAL INTERACTION OF THE MEHANOSYNTHESIZED COPPER COMPOUNDS WITH LIQUID GALLIUM AND ON THE OBTAINED PRODUCT CHARACTERISTICS** S.A. Kovaliova[1], P.A. Vityaz[1], T.F. Grigoreva[2], S.B. Tsybulya[3], N.Z. Lyakhov[2] *[1]Joint Institute of Mechanical Engineering of National Academy of Sciences of Belarus, Minsk, Belarus, [2]Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia, [3]Institute of Catalysis, GK Boreskov, Novosibirsk, Russia*
A083	**THERMOMECHANICAL CHARACTERISTICS OF ARSENIC-SULPHIDE GLASS DOPED WITH BISMUTH** M.V. Šiljegović[1], S.R. Lukić[1], F. Skuban[1], M. Avramov[1], L. Sidjanin[2] *[1]Faculty of Science, Department of Physics, University of Novi Sad, Novi Sad, [2]Faculty of Technical Science, University of Novi Sad, Novi Sad*
A084	**CRYSTALLINE/MAGNETIC STRUCTURE OF $LA_{0.54}PR_{0.11}PB_{0.35-X}SR_XMNO_3$ OBTAINED BY HIGH-ENERGY MILLING** M.-L. Craus[1, 2], N. Cornei[3], I. Zinikovskaia[1], A. Oprea[1, 4] *[1]Joint Institute for Nuclear Research, Dubna, Russia, [2]National Institute of Research and Development for Technical Physics, Iasi, Romania, [3]Chemistry Department, "Al I. Cuza" University, Iasi, Romania, [4]Physics Department, Bucharest University, Bucharest, Romania*
A085	**INFLUENCE OF HIGH-ENERGY MILLING ON THE STRUCTURE AND TRANSPORT PROPERTIES OF $LA_{0.54}HO_{0.11}CA_{0.35}MN_{1-X}CR_XO_3$** A. Oprea[1,2], M.-L. Craus[1, 3], N. Cornei[4] *[1]Joint Institute for Nuclear Research, Dubna, Russia, [2]Physics Department, Bucharest University, Bucharest, Romania, [3]National Institute of Research and Development for Technical Physics, Iasi, Romania, [4]Chemistry Department, "Al I. Cuza" University, Iasi, Romania*
A086	**NON-THERMAL EFFECTS UNDER MICROWAVE HEATING OF SOLIDS AND MATERIALS** A.N. Mikheev *Novosibirsk State University, Nikolayev Institute of Inorganic Chemistry, Novosibirsk, Russia*
A087	**THE SMART PROCEDURE OF NATURAL PRODUCTS ISOLATION** N. Pankrushina[1,2], I. Nikitina[1,2], E. Chernjak[1], V. Boldyrev[1,3] *[1]Novosibirsk State University Novosibirsk, Russia, [2]Novosibirsk Institute of Organic Chemistry, Russia, [3]Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia*
A089	**MECHANOCHEMISTRY AND THE OTHER BRANCHES OF CHEMISTRY: SIMILARITIES AND DIFFERENCES** L. Takacs *Department of Physics, University of Maryland, Baltimore, USA*

A090	**MECHANOCHEMICAL SYNTHESIS OF MgH_2-TiB_2 COMPOSITES FOR HYDROGEN STORAGE** I. Milanović, R. Vujasin, S. Milošević, Ž. Rašković-Lovre, S. Kurko, Lj. Matović, J. Grbović Novaković *Vinča Insitute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia*
A091	**FLUORINE INCORPORATION FROM PTFE TO TITANIA NANOPARTICLES BY COMBINING MECHANICAL STRESSING AND ANNEALING** M. Senna[1], A. Düvel[1], V. Sepelak[2], J. Shi[3], K. DaSilva[1], V. Laporte[4], K.-D. Becker[3], P. Heitjans[1] *[1]Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Hannover, Germany, [2]Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany, [3]Institute of Physical and Theoretical Chemistry, Technische Universität Braunschweig, Braunschweig, Germany, [4]Interdisciplinary Centre for Electron Microscopy, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland*
A092	**SURFACE HARDENED Al ALLOYS PREPARED BY HIGH-ENERGY BALL-MILLING USING VARIOUS PROCESS CONTROL AGENTS** J.-H. Ahn[1], Y.-D. Hahn[2], S. Kim[1], Y.J. Kim[2] *[1]Department of Materials Engineering, Andong National University, Andong, Gyungbuk, Korea, [2]Functional Materials Division, Korea Institute of Materials Science, Seonsan-gu, Changwon, Gyeongnam, Korea*
A093	**EFFECT OF THIRD ELEMENTS ON THE PARTICLE SIZE OF DISPERSOIDS IN MECHANICALLY ALLOYED Ni-Cr-Y_2O_3 ALLOYS** S. Kim[1], J. Jang[2], T.K. Kim[2], J.-H. Ahn[1] *[1]Department of Materials Engineering, Andong National University, Andong, Gyungbuk, Korea, [2]Nuclear Materials Research Division, Korea Atomic Energy Research Institute, Yuseong-gu, Daejeon, Korea*
A094	**STRUCTURAL AND ELECTRICAL PROPERTIES OF Yb SUBSTITUTED Zn-FERRITE OBTAINED BY HEBM** M. Vučinić-Vasić[1], A. Antić[1], B. Antić[2], G. Stojanović[1], A. Meden[3], A. Kremenović[4] *[1]Faculty of Technical Sciences, Novi Sad, Serbia, [2]Institute of Nuclear Sciences "Vinča", Belgrade, Serbia, [3]Faculty of Chemistry and Chemical Technology, Ljubljana, Slovenia, [4]Faculty of Mining and Geology, Belgrade, Serbia*
A095	**CHANGING OF CHELATION ABILITY OF HUMIC ACIDS UNDER MECHANICAL ACTIVATION** S.G. Mamylov[1], O.I. Lomovsky[1], N.V. Yudina[2] *[1]Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia* *[2]Institute of Petroleum Chemistry SB RAS, Tomsk, Russia*
A096	**THE HIGH TEMPERATURE FINE GRINDING OF POLYMERS UNDER ACTION OF INTENSE SHEAR STRESS AS A MECHANOCHEMICAL AVALANCHE-LIKE CRACKING PROCESS OF POLYMERS** A.M. Kaplan, V.G. Nikolskii, N.I. Chekunaev *Semenov's Institute of Chemical Physics RAS, Moscow, Russia*

A097	**EFFECTS OF MECHANICAL ACTIVATION ON THE INTERACTION OF OLIVINE AND VERMICULITE WITH CARBON DIOXIDE** E. Turianicová[1], A. Zorkovská[1], A. Obut[2], Ľ. Tuček[3], Z. Németh[3], P. Baláž[1], İ. Girgin[2] *[1]Institute of Geotechnics, Slovak Academy of Sciences, Košice, Slovakia, [2]Hacettepe University, Mining Engineering Department, Ankara, Turkey, [3]State Geological Institute of Dionyz Stur, Košice, Slovakia*
A098	**MECHANOCHEMICAL PREPARATION AND SOLID-STATE CHARACTERIZATION OF COMPOSITES OF BETULIN AND ITS ETHERS** M.A. Mikhailenko[1,2], T.P. Shakhtshneider[1,2], V.A. Drebushchak[2,3], Yu.N. Malyar[4], S.A. Kuznetsova[4], V.V. Boldyrev[1,2] *[1]Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia [2]Research and Education Center "Molecular Design and Ecologically Safe Technologies" at Novosibirsk State University, Novosibirsk, Russia, [3]Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia, [4]Institute of Chemistry and Chemical Technologies SB RAS, Krasnoyarsk, Russia*
A099	**Fe-Y_2O_3 NANOCOMPOSITE PREPARED BY BALL-MILLING: FORMATION MECHANISMS AND NANOSCALE CHARACTERISATION** F. Legendre[1], M. Brocq[1], M. Couvrat[1], B. Radiguet[2] *[1]CEA Saclay, DEN, DMN, Service de Recherches de Métallurgie Physique, France, [2]Groupe de Physique des Matériaux, Université et INSA de Rouen, UMR CNRS 6634, France*
A100	**MECHANOCHEMICAL PREPARATION OF ORGANIC-INORGANIC HYBRID MATERIALS OF DRUGS** T.P. Shakhtshneider[1,2], S.A. Myz[1,2], N.I. Nizovskii[3], A.V. Kalinkin[3], E.V. Boldyreva[1,2], T.C. Alex[4], R. Kumar[4] *[1]Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; [2]Research and Education Centre "Molecular Design and Ecologically Safe Technologies" at the Novosibirsk State University, Novosibirsk, Russia; [3]Boreskov Institute of Catalysis, Novosibirsk, Russia; [4]National Metallurgical Laboratory, Jamshedpur, India*
A101	**FOLLOWING THE PRODUCTS OF MECHANOCHEMICAL SYNTHESIS STEP AFTER STEP** I.A. Tumanov[1,2] , A.F. Achkasov[1], E.V. Boldyreva[1,2], V.V. Boldyrev[1,2] *[1]Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; [2]Research and Education Centre "Molecular Design and Ecologically Safe Technologies" at the Novosibirsk State University, Novosibirsk, Russia*
A102	**SELECTIVE EFFECT OF CARBOXYLIC ACIDS ON POLYMORPHISM OF GLYCINE AND CO-CRYSTAL FORMATION** E.A. Losev[1,2], M.A. Mikhailenko[1,2], E.V. Boldyreva[1,2] *[1]Research and Education Centre "Molecular Design and Ecologically Safe Technologies" at the Novosibirsk State University, Novosibirsk, Russia, [2]Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia;*

A103	**'HEDVALL EFFECT' IN CRYOGRINDING OF MOLECULAR CRYSTALS. A CASE STUDY OF A POLYMORPHIC TRANSITION IN CHLORPROPAMIDE** T.N. Drebushchak[1,2], A.A. Ogienko[3], E.V. Boldyreva[1,2] *[1]Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; [2]Research and Education Centre "Molecular Design and Ecologically Safe Technologies" at the Novosibirsk State University, Novosibirsk, Russia, [3]Institute of Cytology and Genetics SB RAS, Novosibirsk, Russia*
A104	**DECREASING PARTICLE SIZE HELPS TO PRESERVE METASTABLE POLYMORPHS. A CASE STUDY OF DL-CYSTEINE** V.S. Minkov[1,2], V.A. Drebushchak[1,3,4], A.G. Ogienko[1,4], E.V. Boldyreva[1,2] *[1]Research and Education Centre "Molecular Design and Ecologically Safe Technologies" at the Novosibirsk State University, Novosibirsk, Russia, [2]Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; [3]Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia, [4]Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia*
A105	**MONITORING MECHANICAL PROPERTIES OF INDIVIDUAL HYDROGEN BONDS: SINGLE-CRYSTAL X-RAY DIFFRACTION AND POLARIZED RAMAN SPECTROSCOPY IN SITU** B.A. Zakharov[1,2], B.A. Kolesov[1,3], E.V. Boldyreva[1,2] *[1]Research and Education Centre "Molecular Design and Ecologically Safe Technologies" at the Novosibirsk State University, Novosibirsk, Russia; [2]Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; [3]Institute of Inorganic Chemistry, Novosibirsk, Russia*
A106	**SHS OF SYSTEM WITH ACTIVATED SILUMIN** D.A. Kassymbekova, O.A. Tyumentseva *Institute of Combustion Problems, Almaty, Republic of Kazakhstan*
A107	**PROPOSAL OF A NEW MECHANOCHEMICAL PHASE DIAGRAM FOR THE BINARY SYSTEM Cu-Zn** M.J. Diánez[1], J.M. Criado[1], E. Donoso[2], L.A. Pérez-Maqueda[1], P.E. Sánchez-Jiménez[1], A. Perejón[1] *[1]Instituto de Ciencia de Materiales de Sevilla, Centro Mixto Universidad de Sevilla-C.S.I.C., Sevilla, Spain, [2]Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile*
A108	**SOLVENT-DROP GRINDING SYNTHESIS OF MELOXICAM CO-CRYSTALS** S.A. Myz, T.P. Shakhtshneider, N.A. Tumanov, E.V. Boldyreva *Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Novosibirsk, Russia; Research and Education Centre "Molecular Design and Ecologically Safe Technologies" at the Novosibirsk State University, Novosibirsk, Russia*
A110	**OPTICAL PROPERTIES OF NICKEL MANGANITE CERAMICS OBTAINED FROM MECHANICALLY ACTIVATED POWDERS** S.M. Savić[1], M.V. Nikolić[1], K.M. Paraskevopoulos[2], T.T. Zorba[2], K. Vojisavljević[1] *[1]Institute for Multidisciplinary Research-University of Belgrade, Belgrade, Serbia, [2]Departmant of Physics-Solid State Section, Aristotle University, Thessaloniki, Greece*

A112	**CHARACTERIZATION OF COMPLEX OXIDES PREPARED BY BALL MILLING** M. Fabian[1], S. Suzuki[2], K. Shinoda[2], B. Antić[3], A. Kremenović[3], F. Saito[2], Q. Zhang[2], P. Baláž[1], S. Indris[4], V. Šepelák[4] *[1]Institute of Geotechnics, Slovak Academy of Sciences, Košice, Slovakia, [2]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan, [3]Institute of Nuclear Sciences „Vinča“, Belgrade, Serbia, [4]Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany*
A113	**DEVELOPPING OF MAGNESIUM AND MAGNESIUM-SCANDIUM SYSTEMS WITH OPTIMIZED HYDROGEN SORPTION FOR VLi BATTERIES APPLICATION** M. Kirikova[1], W. Zaïdi[2], J.-P. Bonnet[2], S. Marre[1], C. Aymonier[1], J. Zhang[3], F. Cuevas[3], M. Latroche[3], L. Aymard[2], J.-L. Bobet[1] *[1]Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS), Pessac, France, [2]LRCS, UMR CNRS 6007, Amiens, France, [3]ICMPE, CNRS UMR 7182, Thiais, France*
A114	**MULTIFERROIC PEROWSKITE MATERIALS OBTAINED BY REACTIVE GRINDING** A. Perejón, P.E. Sánchez-Jiménez, M.J. Diánez, J.M. Criado, L.A. Pérez-Maqueda *Instituto de Ciencia de Materiales de Sevilla (CSIC-Univ. Sevilla), Sevilla, Spain*
A115	**ELEMENTARY ENERGETIC AND KINETIC CONSIDERATIONS IN THE MECHANOCHEMICAL SYNTHESIS OF FE-C ALLOYS AND COMPOUNDS** F. Miani, F. Maurigh *DICA University of Udine Italy, Udine, Italy*
A116	**MECHANOCHEMICAL TRANSFORMATIONS IN Ti/B/H_2 SYSTEM** O.S. Morozova[1], T.I. Khomenko[1], A.V. Leonov[2], E.Z. Kurmaev[3], Ch. Borchers[4], I. Prochazka[5] *[1]Semenov Institute of Chemical Physics RAS, Moscow, Russia, [2]Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, Moscow, Russia, [3]Institute of Metal Physics, RAS-Ural Division, Ekaterinburg, Russia, [4]Institute for Material Physics, University of Göttingen, Goettingen, Germany, [5]Faculty of Mathematics and Physics, Charles University in Prague, Praha 8, Czech Republic*
A117	**TO THE PROBLEM OF GENERATION OF NON-EQUILIBRIUM POINT DEFECTS AND ANOMALOUS DIFFUSION IN NANOSTRUCTURES OF METALS DURING MECHANICAL ALLOYING** L.S. Vasil’ev[1], I.L. Lomayev[2] *[1]Physical-Technical Institute, Russian Academy of Sciences, Izhevsk, Russia* *[2]Institute of Quantum Materials Science, Yekaterinburg, Russia*
A118	**THE USING OF SYNCHROTRON RADIATION FOR MECHANOCHEMICAL PROCESS INVESTIGATION: MODEL AND REAL EXPERIMENTS** B.P. Tolochko[1], N.Z. Lyakhov[1], K.A. Ten[2], E.R. Pruuel[2] *[1]Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia* *[2]Institute of Hydrodynamics SB RAS, Novosibirsk, Russia*

A119	**CHARACTERIZATION OF MECHANOSYNTHESIZED NON-EQUILIBRIUM FLUORIDES BY HIGH-RESOLUTION SOLID STATE NMR – CORRELATION OF STRUCTURAL FEATURES WITH IONIC CONDUCTIVITY** A. Düvel, B. Ruprecht, P. Heitjans, M. Wilkening *Institute of Physical Chemistry and Electrochemistry, and Center for Solid State Chemistry and New Materials, Leibniz University Hannover, Hannover, Germany*
A120	**MECHANICAL MILLING OF MAGNESIUM BASED COMPOSITES FOR HYDROGEN STORAGE** I. Milanović[1], R. Vujasin[1], S. Milošević[1], Z. Rašković[1], S. Kurko[1], Lj. Matović[1], J. Grbović Novaković[1], A. Aurora[2], A. Montone[2] *[1]Vinča Insitute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia* *[2]ENEA, UTTMAT Research Centre of Casaccia, Rome, Italy*
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A135	**RAMAN SPECTROSCOPY STUDY OF $NiFe_2O_4$ POWDERS OBTAINED BY SOFT MEHANOCHEMICAL SYNTHESIS** Z.Ž. Lazarević[1], Č. Jovalekić[2], N.Ž. Romčević[1] *[1]Institute of Physics, University of Belgrade, Zemun, Belgrade, Serbia, [2]Institute for Multidisciplinary Research, Belgrade, Serbia*

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A146	**RAPID MECHANO-CHEMICAL REACTIONS DURING ELECTRIC DISCHARGE ASSISTED MECHANICAL MILLING** A. Calka *University of Wollongong, Faculty of Engineering, Wollongong, NSW, Australia*
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A152	**THE PROPERTIES OF THE COMPOSITES SUPPORTED ON STAINLESS STEEL FOIL BY LOW TEMPERATURE IMPLANTATION METHOD** V. Goncharov[1], V. Zazhigalov[2], A. Kowal[3] *[1]Institute of Chemical Technologies of V.Dal' East-Ukrainiane National University, Rubizhne, Ukraine; [2]Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Kyiv, Ukraine; [3]Institute of Non-Ferrous Metals, Central Laboratory of Batteries and Cellls, Poznan, Poland*
A153	**MECHANOCHEMISTRY OF COMPLEX OXIDES** V. Šepelák[1,2], P. Heitjans[3], K.-D. Becker[4] *[1]Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany, [2]On leave from the Slovak Academy of Sciences, Košice, Slovakia, [3]Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Hannover, Germany, [4]Institute of Physical and Theoretical Chemistry, Braunschweig University of Technology, Braunschweig, Germany*

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A157	**ALUMINIUM BASED NANOCOMPOSITES PRODUCED BY BALL MILLING AND HOT EXTRUSION** V.V. Tcherdyntsev[1], S.D. Kaloshkin[1], M.V. Gorshenkov[1], V.D. Danilov[2], V.N. Gulbin[3] *[1]National University of Science and Technology «MISIS», Moscow, Russia, [2]AA Blagonravov Institute of Mechanical Engineering RAS, Moscow, Russia, [3]Sci Res & Design Institute of Assembly Technology, Moscow, Russia*
A158	**MECHANOCHEMICAL LEACHING OF SPHALERITE IN AN ALKALINE SOLUTION** Ch. Zhang, J. Wang, J. Bai, Yuanhao, W. Wu, Y. Zhou *School of Urban Development and Environmental Engineering, Shanghai Second Polytechnic University, Shanghai, China*
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A160	**STRUCTURE FORMATION IN ULTRA IGH MOLECULAR WEIGHT POLYETHELENE AT MILLING TOGETHER WITH ULTRA FINE TUNGSTEN** S.D. Kaloshkin[1], V.V. Tcherdyntsev[1], M.V. Gorshenkov[1], V.N. Gulbin[2] *[1]National University of Science and Technology «MISiS», Moscow, Russia* *[2]Sci Res & Design Institute of Assembly Technology, Moscow, Russia*

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A162	**INVESTIGATION OF COVALENT BONDS USING AFM-BASED SINGLE-MOLECULE TECHNIQUES** S.W. Schmidt[1,2,3], Ch. Glockner[2], P. Filippov[1], A. Kersch[1], M.K. Beyer[2], H. Clausen-Schaumann[1,3] *[1]Munich University of Applied Sciences, Department of Precision- and Micro-Engineering, Engineering Physics, Germany, [2]Christian-Albrechts-Universität zu Kiel, Institut für Physikalische Chemie, Germany, [3]Ludwig-Maximilians-Universität München, Center for NanoScience (CeNS), Germany*
A163	**NMR STUDIES IN MECHANOCHEMISTRY** P. Heitjans[1], A. Düvel[1], B. Ruprecht[1], M. Wilkening[1], V. Šepelák[2] *[1]Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Hannover, Germany; [2]Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany*

Abstracts

A001

PIV MEASUREMENT OF THE SHELL SIDE FLOW CHARACTERISTICS OF SHELL-AND-TUBE LNG VAPORIZER

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Shell-and-tube heat vaporizers are among the most commonly used and dominated types of vaporizers in LNG realm. Shell-side flow in this type of vaporizer has received considerable attention and has been investigated extensively. However, the detail flow structure in the shell needs to be determined for reliable and effective design. Therefore, the objective of this study was to clarify the flow structure in shell by particle image velocimetry (PIV). Experiments were conducted using two types of model; 15% baffle cut having inlet and outlet positions in the direction of 90^0 to the cut and 30% baffle cut having inlet and outlet positions in the direction of 180^0 to the cut. Each test section contains 169 mm I.D. and 344.6 mm length. The flow features were characterized in different baffle cuts with regards to the velocity vector field, vortex structure, stream line and turbulent intensity.

Keywords: PIV (Particle Image Velocimetry); LNG (Liquefied Natural Gas); Vaporizer; Vortex, Turbulence

A002

PROCESSING OF EGGSHELL BIOMATERIAL BY HIGH ENERGY MILLING AND EDAMM TECHNIQUES

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Hen eggshell biomaterial typically consists of $CaCO_3$ (94%), $MgCO_3$ (1%) and organic matter (4%). The by-product eggshell generated from food processing and manufacture plants is inevitably composed of calcium carbonate (eggshell, ES) and eggshell membrane (ESM).

Here we show that ES after processing by electric discharge assisted mechanical milling (EDAMM,[1]) and/or high energy milling (HEM, [2]) techniques transform to new materials suitable for advanced applications. Physical and chemical changes induced by EDAMM and HEM techniques were examined by XRD, low-temperature nitrogen absorption, SEM, FT-IR, thermal analysis, sorption and reactivity measurements.

EDAMM treatment of ES resulted in mechanochemical transformation of calcium carbonate (calcite, JCPDS card 47-1743) to CaO (lime synthetic, JCPDS card 04-0777) according to reaction:

$$CaCO_3 \xrightarrow{EDAMM} CaO + CO_2$$

HEM treated samples showed high degree of bulk amorphization (88%) and enhanced specific surface area (20.9 m^2g^{-1}) in comparison with 2.2 m^2g^{-1} for untreated sample. Several heterogeneous post-processes like decomposition of organics and sorption of cadmium ions from solutions were tested to illustrate the extraordinary properties of ES after treatment by EDAMM and HEM techniques.

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A003

NEW INSIGHTS INTO THE MECHANISM OF PHOTOINDUCED, THERMALLY INDUCED AND MECHANICALLY INDUCED EFFECTS IN MOLECULAR CRYSTALS

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Understanding of the fundamental physicochemical processes in photoactive materials requires detailed knowledge of the related changes in their structure at atomic, molecular and supramolecular level. During the last several years, in our laboratory we have been developing several X-ray diffraction (XRD) techniques, which were utilized in combination with other analytical (microscopic, spectroscopic, thermoanalytical and theoretical) methods to study, at atomic-scale resolution, the structural perturbations induced in a variety of small-molecule crystalline materials by utilizing light excitation, changes in temperature, or other external stimuli. Typically, a technique which we have employed in such studies was steady-state/time-dependent and variable-temperature X-ray single crystal/powder photodiffraction (photocrystallography). The results have provided direct insight into the structures of unstable species and fundamental dynamic solid-state phenomena. This talk will summarize our recent results with these techniques applied on several solid-state systems which are of importance for electronics/spintronics, nanotechnology, medical and bioanalytical applications. In particular, the results include photodimerizations, gradual/sharp phase transitions, thermosalient (jumping) effects of crystals, photomechanical effects, solid-state rearrangements, unstable biological molecules, photomagnetization effects and photoinduced phase transitions of persistent organic radicals, unstable radical transients or uncommon radical states, photochromic and thermochromic species, and other systems.

A004

“GIANT MAGNETIC FULLERENES” AS A NANOPLATFORM TO REALIZE THE MULTIMODAL SYSTEMS FOR MEDICAL AND TECHNICAL APPLICATIONS

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The combination of advanced nanotechnology, organic chemistry, molecular biology and the increasing availability of physics-technical instruments opens new perspectives for design of multifunctional systems for different applications. The most attractive and less studied objects are “core-shell” structure, such as magnetic metals (Fe, Co, Ni and others) in a nanocrystalline state covered by carbon as a stable platform for multimodal purposes. For instance, nontoxic and biocompatible nanocomposites with the structure of magnetic “iron core-carbon shell” as a “Giant Magnetic Fullerenes” (GMF) can be considered as a multimodal platform on which would be located simultaneously the targeted biomolecules (synthetic peptide-analogues of fragments of protein active centers), polymer ligands providing the stability of systems in biological medium and radiopharmaceutical agents with diagnostic and therapeutic functions. After original synthesis the nanocomposites represent “metal core-carbon shell” structure with the average size of less than 10 nm. Structural parameters of metal-carbon nanocomposites have been studied by X-ray diffraction analysis, high resolution transmission electron microscopy, XPS, XAS, Raman and Mossbauer spectroscopy methods. The observed Raman spectra of metal-carbon nanocomposites allow us to make a conclusion that the carbon coating is not perfectly complete (like fullerene structure) but those are organized from fragments of graphene planes with sizes of 10 nm lengthwise. The unusual magnetic properties of Fe encapsulated in carbon and structural transformation in the nanoscale range (size less than 10 nm) were revealed and discussed as well. We developed a new and straightforward method for the covalent modification of the surfaces of metal nanoparticles (Me@C) coated by carbon by applying aryldiazonium tosylates (ArN_2^{+-} OTs). This method makes it possible to obtain the organic reactive groups (COOH, NO_2, NH_2) on the surface of nanosized materials which are potentially suitable for the covalent immobilization of various biomolecules and ligands. Magneto-controlled radiopharmaceuticals based on Fe@C particles grafted ^{99}Tc isotopes have been obtained which can be successfully used for combined medical diagnostics (MRI, gamma-camera). In summary the nanocomposites on the base of different metals encapsulated in carbon present a novel class of stable nanomaterials possessing the unique physical, chemical properties and biological properties for promising practical applications in medicine and technical applications.

We express our gratitude to RFBR (grant №10-02-00323) for their financial support.

A005

MECHANOCHEMICAL SYNTHESIS OF CARBON NANOMATERIALS BY A HIGH-SPEED BALL-MILLING PROCESS

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A novel mechanochemical approach inspired by the Allende meteorite to produce sophisticated carbon nanomaterials is reported. It is demonstrated that unique carbon nanostructures, including carbon nanotubes, carbon onions, and new carbon nanorings are synthesized by high-speed ball-milling of steel balls. The carbon nanorings have diameter of several ten nanometers. It is considered that the gas-phase reaction takes place around the surface of steel balls under local high temperatures induced by the collision energy in ball-milling process, which results in phase separated unique nano-carbon materials. This paper also shows the mechanochemical synthesis of fine nanoparticles of Fe based complex oxide by the high-speed ball-milling process.

A006

ARSENIC MECHANOCHEMISTRY: FROM MINERALS ENGINEERING TO CANCER TREATMENT

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The driving force for the increased interest in arsenic compounds research is new physics, chemistry and medicine. Here novel applications are expected in the near future. However, the arsenic mechanochemistry plays also the crucial role in various processes of traditional extractive metallurgy.

This contribution will illustrate the progress in "traditional" as well as "advanced" aspects of arsenic mechanochemistry.

In extractive metallurgy of arsenic the special attention will be given to results of thermal dearsenification of mechanically activated arsenopyrite FeAsS, mechanochemical and bacterial leaching of tetrahedrite-tennantite $Cu_{12}(Sb,As)_4S_{13}$ and enargite Cu_3AsS_4. In this case dearsenification of industrial minerals improves selective extraction of most of the metal values from the complex sulphide cocentrates. The environmental aspects of the mechanochemical processing are especially important [1].

In traditional Chinese medicines, different forms of mineral arsenicals like orpigment As_2S_3, realgar As_4S_4 and arsenolite As_2O_3 are used. Realgar has been used in traditional Chinese medicine externally or even orally to treat psoriasis, syphilis and malaria. However, its broader healing effect was documented recently also in cancer treatment [2]. The possibility to synthesize realgar nanoparticles by mechanochemical means brings new opportunities for studying its applications in new therapeutic strategies. By decreasing particle size, the drug can be readily taken up by cells because of an increase surface to volume ratio. This allows a faster drug release into cells and increase of bioavailability. Several examples of various cancer cell lines treatment with realgar nanosuspensions will be given to illustrate the effect of media milling process.

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A008

INFLUENCE OF VOLUME FRACTION ON SUPERPLASTIC DEFORMATION OF Al-Al_4C_3 SYSTEM PREPARED BY MECHANICAL ALLOYING

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Superplasticity in polycrystalline materials is facilitated by dynamic modifications in the microstructure. Influence of mechanical milling parameters and deformation on superplastic deformation was observed on Al-Al_4C_3 system with different vol.% of Al_4C_3, (4 and 12 vol. %). The milling of the Al powder (grain size less than 50 μm) with 1 and 4 % of KS 2.5 graphite lasted 90 minutes. Granulate was compacted under the pressure of 600 MPa and annealed at 550 °C during 3 hours with the aim to transform C to Al_4C_3. Hot extrusion of rods was performed at 600°C with a 94% reduction. The residual porosity of this material was up to 1%. The size of dispersed phase particles measured on TEM was ~30 nm and grain size was ~380 nm. The material was tested at temperatures from 20 to 450 °C and strain rates from $\dot{\varepsilon} = 2.5\cdot10^{-5}\ s^{-1}$ to $1\cdot10^{-1}\ s^{-1}$. The tensile test specimens were oriented in longitudinal direction, in respect to the direction of extrusion. We suppose the deformation of the Al-Al_4C_3 system was combined and included: dynamic polygonization by dislocation migration and annihilations, slip on grain boundaries, displacement of grains by rotation, partial recrystallization causing grain boundary movement of polygonized grains, dislocation creep, causing accommodations of defects on grain boundaries. Grains can move or be reordered by two mechanisms: slip along grain boundaries and rotation. For low dispersed phase particle content (4 vol.% of Al_4C_3) and at strain rate $1\cdot10^{-1}\ s^{-1}$ the elongated grains and slip on grain boundaries are more frequent, with lower probability of polygonization and partial recrystallization. We suppose that at high strain rate $1\cdot10^{-1}\ s^{-1}$ and high dispersed phase content (12 vol.% of Al_4C_3) dynamic recovery is started by the high accumulated deformation energy, first dynamic polygonization of grains, repositioning by rotation (no elongated grains seen), partial recrystallization and dislocation creep can take place, too. Clusters of particles identified as Al_4C_3 on grain boundaries suggested more rotation than slip. For the description of the overall effect of temperatures and deformation rates on stress at 0.2% permanent deformation, the parameters of the mechanical equation of the state used for materials with 12 vol.% of Al_4C_3 subjected to high stresses according to Poirier were determined: $\varepsilon\cdot\exp(Q/RT)=3.15\cdot10^{13}\cdot\exp(-0.152\cdot R_{p0.2})$. Here is included the value of Zener-Hollomon parameter in the temperature region 300-500 °C in the investigated interval of deformation rate. Its correlation coefficient r = 0.953 suggests a certain scatter of material properties. The apparent activation energy reached the value 325 kJ.mol^{-1}.

A009

EVOLUTION OF ELECTRON STRUCTURE AND THERMODYNAMICS OF NANOSTRUCTURED COMPOSITES AT MECHANICAL ACTIVATION

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Results of study of an electronic structure of valent band of nanostructured of Fe-Bi- and WC-Ti composites are submitted. Fe-Bi-composites were received by Lyakhov N. et al. in 2004. They represent significant interest. Ilyasov V. with the colleagues has carries out *ab-initio* accounts of total energy, band structure and thermodynamics of system Fe-Bi. The band structure calculations of composites were performed using the plane-wave pseudopotential method within the framework of DFT (Quantum Espresso). All calculations were based on the σ-GGA spin collinear approximation, using the PBE expression for the exchange-correlation functionals. Various structural positions of atom Bi in Fe-Bi system are investigated. Energy interpretation of the mechanism of formation of a nanostructured superficial layer is given. Laws of change of atomic and electronic structures are discussed.

A010

SYNTHESIS OF FINE $Ni_{75}Mg_{16.66}Y_{8.34}$ (at %) POWDER FOR USING AS A CATALYST BY SOLID REACTION AND MECHANICAL MILLING

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$Ni_{75}Mg_{16.66}Y_{8.34}$ can be used as a catalyst for improving the hydriding properties of solid state hydrogen storage materials such as MgH_2. In this study, fine $Ni_{75}Mg_{16.66}Y_{8.34}$ powder was prepared by two methods. In the first method, the pure elemental powders were subjected to high energy ball milling for 5 to 25 hrs with ball to powder weight ratio of 20. In the second method the elemental powder pressed, heat treated at 800 ºC for 4 to 10 hrs (solid reaction) and then ball milled at similar condition to the first method. Finally, phases and particle size of prepared alloys were investigated by XRD, SEM, and particle size analyzer. The XRD results showed that Mg_2Ni_9Y ternary intermetallic phase was formed only by the second method. Moreover, the particle size of prepared alloy by second method was 5-10 μm while, it was 20-25 μm for powders prepared by first method. Therefore, it was concluded that the $Ni_{75}Mg_{16.66}Y_{8.34}$ powder with particle size of less than 10 μm and high Mg_2Ni_9Y content for using as a catalyst could be prepared by pressing, solid reaction during heat treatment and subsequently, ball milling.

Keywords: Ball milling, Mechanical alloying, Mg_2Ni_9Y, Solid reaction, Catalyst, Hydrogen adsorption.

A011

STRUCTURAL TRANSFORMATIONS IN TITANIUM UNDER MILLING IN A PLANETARY MILL IN THE PRESENCE OF NONMETALLIC CARBON AND BORON ADDITIVES

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The work is devoted to investigation of structural transformations in titanium under milling in the presence of nonmetallic carbon and boron additives in a planetary mill AIR. Interpretation of the obtained XRD patterns made it possible to conclude that at the beginning of milling under impact loads and shear deformation, carbon incorporates into the titanium lattice and forms interstitial solutions whereas boron forms substitution solutions, which results in significant strains and distortions. With achieving certain limit values of strain, a phase transition occurs through collective move, due to which the strains disappear and a new phase (TiC or TiB_2) is formed with slight distortions. The diffusionless phase transition through collective move is possible thanks to the correspondence of the dense-packed planes of Ti (002) to TiC (111) or Ti (002) to (001) TiB_2.

A012

ENERGY TRANSFORMATIONS IN A CENTRIFUGAL AND PLANETARY GRINDING MILLS

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Mechanical activation is an innovative procedure where an improvement of chemicals and row reactivity increasing can be attained via a combination of new surface area and formation of crystalline defects in minerals. The lowering of reaction temperatures, the increase of rate and amount of solubility, preparation of water soluble compounds, the necessity for simpler and less expensive reactors and shorter reaction times are some of the advantages of mechanical activation.

Since a study of mechanical activation phenomena is a very important problem in this paper the efficiency of energy transformation of different kind of matter (CaO_2, BaO_2, Si, $BaTiO_3$, glass) in centrifugal and planetary grinding mills was considered. By differential thermal analysis it was established that dry milling in a centrifugal and planetary grinding equipments leads to accumulation of essential energy by crystal lattice. The energy stored in these mechanically activated defects of structure for a long time and form metastable states. On the differential thermal analysis curves for mechanically activated samples the sharp exothermal peaks were observed. The form and intensity of them depend on nature of powder, treatment duration and type of grinding mills. It was found that grinding in centrifugal grinding mill leads to forming the sharp and intensive exothermal peaks on differential thermal analysis curves. At the same time the grinding in planetary grinding mills leads to the appearance of more slightly peaks with a little intensity. The formation of mechanically induced metastable states for crystals is accompanied by XRD line broadening and appearing of microdeformations and block size changing. Data can be used for clearing of structural imperfections generation mechanism and establishing of correlations between thermodynamic and structural parameters and study of chemical bond and geometry role of mechanically activated compounds lattice.

A013

EFFECT OF NANO-STRUCTURED STATES FORMATION IN ION-IRRADIATED Pt

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The effect of formation nanocrystalline structures in subsurface volumes of platinum in result of implantation accelerated up to 30 keV positive ions of argon (F = 10^{16}-10^{18} sm^{-2}) is established by FIM. The method allows analyzing the object of research in volume by controlled and sequential removal of surface atoms by an electric field at cryogenic temperatures. This phenomenon is observed on distances not less, than 60 nm from the irradiated surface of metal (at F = 10^{18} sm^{-2}). The sizes of nanoblocks (nanograins) both on irradiated surface Pt, and in subsurface volume of a material are certain. Work is executed with support of the federal target program «Scientific and scientific and pedagogical cadres of innovative Russia» for 2009-2013 (N П831) and of the Ural branch of the Russian Academy of Sciences OFN program of RAS № 5 «Physics of new materials and structures».

A014

MECHANISMS FOR MECHANICAL SYNTHESIS OF ODS ALLOYS USING LOW-STABILITY IRON OXIDES

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One of actual problems facing the development of the nuclear power engineering is an insufficient radiation resistance of pressure vessel steels, which are used specifically for fuel element shells. So far the promising materials in this respect are ODS steels, which are traditionally produced by breaking of coarse (30-40 μm) stable oxides like Y_2O_3 to a fine fraction (2-4 nm). We have proposed a fundamentally new approach to the production of ODS steels. This approach is based on mechanical alloying with low-stability iron oxides, which enter into the metal matrix during cold deformation and, in this way, introduce oxygen atoms into this matrix. The subsequent annealing of the steel, which has been mechanically alloyed with oxygen, leads to the precipitation of hardening stable yttrium (titanium) nanooxides, which have been added to the steel beforehand. The aim of this work was to study processes involved in a mechanical synthesis of low-stability iron oxides in matrices of metals and steels and investigate the formation of stable nanooxides of yttrium and titanium during mechanical synthesis and subsequent annealing. The mechanical synthesis (MS) included grinding of the initial mixtures in a Pulverisette-7 planetary ball mill in an inert argon medium. The processes involved in the mechanical synthesis of ODS alloys with bcc and fcc lattices were studied in experiments, in which the initial mixture was powders of alloys based on iron (Fe-Y-Ti, Fe-13.5Cr-2W-Y-Ti) and invars (Fe-Ni-Ti, Fe-Ni-Zr) with special alloying (Ti, Y, etc.), which were mixed with hematite in the ratio of 30 mass % α-Fe_2O_3 and 70 mass % alloy. The structural characteristics of the materials under study and the parameters of their behavior kinetics under deformation were studied mostly by the method of Mössbauer spectroscopy, along with an X-ray diffraction analysis and the method of electron microscopy. The investigations showed that the intensity of dissolution of iron oxides in pure metals (Fe, Ni, Ti, and Zr) and alloys based on Fe (Ni, Ti and Zr) under deformation is determined by oxidizability of the matrix metal. A severe deformation of metal-oxide mixtures leads to decomposition of low-stability oxides, dissolution of iron and oxygen in the metal matrices, and development of an alternative process involving precipitation of secondary oxides. dispersed oxides Y_2O_3, TiO_2 and Y_2TiO_5. An analysis of the diffusion processes taking place during an intensive deformation of powdered mixtures of iron oxides and doped alloys demonstrated that analogous processes occur in iron alloys with bcc and fcc lattices. Dissolution of the initial low-stability oxides is followed by the formation of metallic solid solutions and secondary nanooxides of alloying Y, Ti, and Zr both immediately under deformation and during the subsequent high-temperature annealing.

A015

LOW TEMPERATURE ATOM MASS TRANSFER IN STEELS AND ALLOYS AT INTENSIVE PLASTIC DEFORMATION

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The results of large investigation cycle on nonequilibrium diffusion phase transitions in steels and alloys at intensive cold deformation are presented. Rolling, compression shear in Bridgman anvils and ball mill processing were used as the methods of plastic deformation. The research have investigated phase transitions mechanisms – processes of redistribution of alloying elements, dissolution and formation of intermetallics, carbides, nitrides and oxides in steel matrixes, which can be explained by the generation of large amount of linear (dislocations) and point (vacancies and interstitial atoms) defects of deformation origin.

A016

MECHANOMAKING OF NANOSTRUCTURE IN NITRIDED Fe-Cr ALLOYS AT INTENSIVE PLASTIC DEFORMATION

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Mechanomaking of supersaturated metal solid solutions and composites is actively used for the development of nanostructurized materials, for example, steels and alloys strengthened with oxides. It is very difficult and sometimes impossible technologically to obtain high concentration of nitrogen in solid solutions of metal and alloys by the common metallurgical way. As alternative to metallurgical methods, the new approaches for using mechanical activation for nitration of iron alloys have appeared recently. Mechanical nanostructurization was applied in works using the nitrided by ion-plasmic (IP) method iron surface as an example. The process enclosed the deformation-induced dissolution by IP method of nitrides (Fe_4N and TiN) on the iron surface and extraction of secondary nanocrystal nitrides. The methods of Mossbauer spectroscopy, X-ray diffraction analysis and electron microscopy were used in this research to study the processes of formation of nitrogen supersaturated solid solutions and nanostructurization of nitrided with IP method Fe-Cr and Fe-Cr-Ni alloys surface using mechanical activation by compression shear in Bridgman anvils. It is shown that IP nitration of steels leads to the formation of disperse nitrides Fe_4N and CrN in metal matrixes. In result of deformation the dissolution of nitrides, the formation of nitrogen supersaturated α (BCC) and γ (FCC) solid solutions and the fragmentation of metal matrix structure were observed. FCC phase is enriched with nitrogen in introduction positions to 10 and more at. %. The following annealing leads to the formation of secondary nanonitrides which limit the growth of matrix grains and stabilize the formed nanostructure.

A017

THE EFFECT OF THE COLD PLASTIC DEFORMATION RATE ON INTERMETALLICS DISSOLUTION INTENSITY IN AUSTENITIC Fe-Ni-Me (Ti, Al, Zr, Si) ALLOYS

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Deformation rate as a critical parameter of the process of anomalously low-temperature deformation-induced diffusion in metals is investigated for high rates $\acute{\varepsilon} = 10^2 \ldots 10^3$ c^{-1}, for example, at impact or impulse action. It is supposed, that in such cases the tension in structure reaches such magnitudes which promotes the generation of interstitial positions that take part in low-temperature nuclear mass transfer. It was established that at low rates $\acute{\varepsilon}$ in the interval $10^{-2} \ldots 10^{-1}$ c^{-1}, but at larger degrees $\varepsilon = 4 \ldots 7$ of deformative influence under compression shear in Bridgman anvils the increase of rotation rate in anvils from 0.3 to 1 rpm leads to large (about 30%) intensification of dissolution of intermetallic particles Ni_3Me (Me = Ti, Al, Zr, Si) in matrix of FCC Fe-Ni alloys. The method of Mossbauer spectroscopy was used to determine the dissolution kinetics by the growth of effective magnetic field on nuclei ^{57}Fe as a result of growth of nickel content in matrix at intermetallics dissolution. The kinetic curves of dissolution of particles with different morphology, sizes, crystal lattice type, bonding forces and diffusion atom mobility were obtained. The rate influence is mostly exhibited on the steep part of kinetic dependence of ΔC_{Ni} on ε, when the rotation mode of deformation dominates. It is specified, that kinetics of deformation-induced nonequilibrium phase transitions is controlled by the competitive development of alternative processes of phase dissolution and extraction. The increase of slope angle of kinetic dissolution curves happens mainly because of the influence time shortening of alternative process of intermetallics extraction over vacancy mechanism, and apparently because of the concentration growth of interstitial atoms which take part in the nonequilibrium dissolution of intermetallics. Besides, it is shown that the increase of deformation rate is accompanied by reduction of deformation incubation period ε_0, necessary for the preliminary particles splitting. The obtained results have practical importance for the development of steels and alloys strengthened with nanodimensional particles with the use of mechanical activation.

A018

POSSIBILITIES OF EXCHANGE MECHANOCHEMICAL REACTIONS FOR PREPARATION OF DISPERSE CERAMIC MATERIALS

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Exchange reactions proceeding under the conditions of mechanical activation are widely used to obtain nanometer-sized particles of oxides and oxide materials. The synthesis process includes the interaction of salts of different metals. The salts which formed during the synthesis, are the matrices preventing the particles of the target reaction oxides from aggregation. The target products and initial products tracers are separated from the matrices by dissolving them in water, ethanol and other solvents. The goal of the present work is to establish the possibilities of solid-phase exchange reactions for obtaining dispersed silicates of aluminium, magnesium and solid solution ZrO_2-Y_2O_3, which are widely used in ceramic industry.

To obtain dispersed powder of mullite, we proposed a solid-phase exchange reaction of aluminium chloride with sodium silicate in the presence of sodium hydroxide; the reaction proceeds under mechanical activation. Mechanical activation of a mixture of aluminium chloride $AlCl_3 \cdot 6H_2O$, sodium metasilicate $Na_2SiO_3 \cdot 9H_2O$ (at the ratio Al/Si=6/2) and sodium hydroxide NaOH is accompanied by the formation of X-ray amorphous product and a well crystallized sodium chloride with the lattice parameter 0,563(6) nm, microdeformation $\Delta\alpha/\alpha$,=0,18%, crystallite size 84 nm. The fact that the reflections of sodium chloride appear in the diffraction patterns is an unambiguous evidence of the exchange reaction between the components going during activation. Further thermal treatment was carried out only with the X-ray amorphous reaction products (washed from sodium chloride). At the calcination temperature of 750 ^oC, some indixes of the formation of mullite $Al_6Si_2O_{13}$ appear in the diffraction patters of these samples; mullite is reliably registered at a temperature of 1000 ^oC. An increase in calcination temperature up to 1200 ^oC is accompanied by an increase in crystallite size but has no effect on lattice parameters.

Mechanical activation of the mixtures of magnesium chloride $MgCl_2.6\ H_2O$ with sodium metasilicate $Na_2SiO_3 \cdot 9H_2O$ was carried out in a similar manner. Subsequent thermal treatment resulted in obtaining magnesium silicates (forsterite Mg_2SiO_4 and enstatite $MgSiO_3$).

Mechanical activation of mixture of zirconium oxynitrate $ZrO(NO_3)_2 \cdot 3H_2O$ with yttrium carbonate $Y_2(CO_3) \cdot H_2O$ followed by thermal treatment of this mixture results in the formation of solid solution ZrO_2–Y_2O_3 at temperature 600 ^oC.

Relatively low temperature of product crystallization after the activation of mixtures allows obtaining finer dispersed powders. The specific surface of mullite samples calcined at 1000 ^oC is equal to 16 m^2/g. Mullite density equal to 3,16 g/cm^3, the size of globules of these samples is about 120 nm. So, mechanochemical exchange reactions can be proposed as a method to obtain finer dispersed oxide powders.

A019

NANOSTRUCTURE AND PHASE FORMATION IN METALLIC SYSTEM UNDER MECHANICAL ALLOYING

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So far, the mechanism of phase formation under mechanical alloying and grinding is a subject of extensive studies. The results on nanostructure formation, mechanical alloying of Fe-based binary systems with interstitial (B, C), substitutional (Al, Si, Ge, Sn), immiscible (Mg) elements, of Mo/8at.%O composite with 1 at% ^{57}Fe are presented in this report. The following scheme of nanostructural formation is considered: increasing of dislocation density → polygonization → dislocation pile-up → dynamic recrystallization (grain size $L\approx100$ nm) → deformation twinning and polymorphous transformation ($L\leq10$ nm). A term of interface in nanostructure is defined as the area including boundary and close-to-boundary distorted zones. The widths of interface and boundary have been estimated to be equal of about 1 and 0.2 nm, respectively. It has been established that solid-state reactions under severe mechanical treatment begin on condition that Fe and Mo reaches a nanostructural state. The next stage includes penetration of the second component (B, C, Al, Si, Ge, Sn, ^{57}Fe) atoms along grain boundaries of metals and its segregating at boundaries. This segregation is the source to form the first phase in interfaces. Depending on the type of the second component, different phases can be formed: intermetallic compounds, supersaturated solid solutions and amorphous phases. Possible mechanisms of the low-temperature accelerated mass transfer are discussed.

A020

CORROSION STUDY AND SURFACE CHARACTERIZATION OF SOME PROCESS VARIABLES ZINC PLATED MILD STEEL IN HCL SOLUTION

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This work investigates the feasibility of the effect of some essential plating variable of zinc coating on low carbon steel substrates. The results showed overall improved surface finished properties with different coating depth due to the variation of plating parameter, the depth of immersion, distance between the anode and the cathode on voltage, plating time and coating thickness. The steel substrates were immersed into solution of zinc electroplating bath for varying voltage between 0.5 v and 1.0v. It was discovered that the sample plated at 0.8V for 20 minutes gave the best plating properties. In addition the increase in applied voltage, plating time, depth of immersion and decrease in distance of the object (cathode) from the anode, gave increase in weight gained and coatings properties. The characterization of plating was carried out by scanning electron microscopy (SEM) and X-ray diffraction.

A021

ANTIMICROBIAL AND ANTIOXIDANT ACTIVITIES AND PHYTOCHEMICAL SCREENING OF THE PLANT *KITAIBELIA VITIFOLIA*

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This study was aimed at evaluating the antioxidant activity and efficacy of the ethanolic extract of the endemic plant species *Kitaibelia vitifolia* in inhibiting the growth of selected fungi and bacteria. Antimicrobial activity was tested using broth dilution procedure for determination of minimum inhibitory concentration (MIC). MICs were determined for 8 selected indicator strains. The highest susceptibility to *Kitaibelia vitifolia* ethanolic extract among the bacteria tested was exhibited by *B. subtilis* ATCC 6633*, S. aureus* ATCC 25923 and *K. pneumoniae* ATCC 13883 (MIC = 15.62 µg/mL), followed by strains of *E. coli* ATCC 25922 and *P. mirabilis* ATCC 14153 (MIC = 31.25 µg/mL), and *P. vulgaris* ATCC 13315 and (MIC = 62.50 µg/mL). Among the fungi, *C. albicans* ATCC 10231 (MIC = 15.62 µg/mL) showed the highest susceptibility, and *A. niger* ATCC 16404 (MIC = 31.25 µg/mL) the lowest. Results showed that *Kitaibelia vitifolia* extract possesses antioxidant activity, with total antioxidant capacity of 75.45±0.68 µg AA/g and IC50 values of 47.45±0.55 µg/ml for DPPH free radical scavenging activity, 35.35±0.68 µg/mL for inhibitory activity against lipid peroxidation, 95.25±0.52 µg/mL for hydroxyl radical scavenging activity and 31.50±0.35 µg/mL for metal chelating activity. Total phenolics, flavonoids, condensed tannins and gallotannins were 85.25±0.69 mg GA/g, 45.32±0.55 mg RU/g, 54.25±0.75 mg GA/g and 41.74±0.55 mg GA/g, respectively. The phenolic composition of *Kitaibelia vitifolia* extract was determined by HPLC method. Rosmarinic acid was found to be the dominant phenolic compound of the extract.

Keywords: antimicrobial activity, antioxidant activity, HPLC analysis, Kitaibelia vitifolia.

A022

DEFORMATION OF GRAPHENE AND ITS CHEMICALLY MODIFIED ANALOGUES AS MECHANOCHEMICAL REACTION

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The response of a nanographene sheet to external stresses is suggested to be considered in terms of a mechanochemical reaction. The quantum chemical realization of the approach is based on the coordinate-of-reaction concept by introducing mechanochemical internal coordinates (MICs) that specify the deformational mode. The related forces of response are calculated as the energy gradient along the MICs, while the atomic configuration is optimized over all of the other coordinates under the MICs constant-pitch changing. The approach has been applied to nanographene and nanographane sheets subjected to uniaxial tension. As shown, a high stiffness of both bodies is connected with that one of the relevant benzenoid units. The anisotropy of the units mechanical behavior in combination with different packing of the units either normally or parallel to the body C-C bond chains forms the ground for the structure-sensitive mechanism of the mechanical behavior that drastically depends on a particular deformation modes. The mechanical behavior of graphene under *zg* and *ach* deformation modes is similar to that of a tricotage when either the sheet rupture has both commenced and completed by the rupture of a single stitch row (*ach* mode) or the rupture of one stitch is 'tugging at thread' the other stitches that are replaced by still elongated one-atom chain of carbon atoms (*zg* mode). Hydrogenation of the pristine graphene noticeably influences both behavior and numerical characteristics of the body making tricotage-like pattern of the graphene failure less pronounced. The intimate connection of the bodies behavior with the benzenoid structure opens possibility to predict the behavior of chemically modified graphene by studying mechanical behavior of the corresponding molecules, such as hexamethylene benzene, hexamethyl cyclohexane, hexamethyl hexafluoro cyclohexane, and hexamethylene cyclobornitrid that constitute the methylene- and/or methyl-framed hexagon patterns of pristine and chemically modified graphenes as well as of their bornitrid analogue. Actually, as shown, the Young moduli of the molecules are well consistent with experimental data related to graphene, graphane $(CH)_n$, graphene fluoride $(CF)_n$, as well as to bornitrid analogue $(B_3N_3)_n$. The quantum-mechanochemical-reaction-coordinate approach has disclosed atomically matched peculiarities that accompany the deformation-failure-rupture process occurred in the bodies. For the first time, the approach makes allowance for tracing deformation-stimulated change in the chemical reactivity of both nanographenium sheets and their individual atoms in terms of total and partial numbers of effectively unpaired electrons.

A023

MECHANYCALLY ACTIVATED ENZYMATIC HYDROLYSIS OF YEAST CONTAINING BIOMASS FOR RECYCLING OF INDUSTRY WASTES

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Mechanycally activated enzymatic hydrolysis of yeast biomass is demonstrated to serve as the basis for the development of the technology of obtaining prophylactic preparations containing mannanoligosaccharides in biologically available form. As a result of mechanical activation and enzymatic hydrolysis of yeast biomass, the concentration of available mannanoligosaccharides in the final product is 3.8 %, which is 2.9 times higher than that in the initial biomass. Biological tests showed that the developed mannanoligosaccharide additives have a positive effect on the live weight and gross liveweight gain of experimental animals. The use of the ethanol, beer or food industry wastes as the raw material containing yeast, and feeding with thus obtained preparation will allow poultry farms to gain additional profit.

A024

INCONSISTENCIES OF SOLID SURFACE STRESS DEFINITIONS IN LAGRANGIAN AND EULERIAN DESCRIPTIONS

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Mechanochemistry of solids includes the study of thermodynamic, chemical and mechanical properties of the surfaces of deformable bodies and among them one of most disputable up today is a thermodynamic definition of the surface stress. In this lecture serious mathematical defects in the applications of rational mechanics to the solid surface stress problem will be shown. Also it is shown that rough handling with the Lagrangian and Eulerian descriptions leads to the famous, but erroneous Shuttleworth's equation which must be removed from use. As it is known the outstanding result of Gibbs theory is the Gibbs-Duhem equation that is the relationship between differentials of the intensive thermodynamic variables. However, the errors made during the derivation of the Shuttleworth equation have led to the distortion of the Gibbs-Duhem equation by extensive variables and the result cannot bear the name Gibbs-Duhem despite many of authors call it so. Nevertheless, persistent attempts were made by the different authors to prove the Shuttleworth equation applying Eulerian/Lagrangian coordinate transformations to the usual 2D definition of a stress tensor taken from the theory of elasticity. But in their procedures containing the same fundamental errors as above mentioned (explicitly or implicitly), additionally new mistakes were made. Moreover, the approach of Gibbs to the surface stress problem is not needed in the application of methods of rational mechanics because this problem is limited to the region of small deformations where the Eulerian and Lagrangian descriptions are practically indistinguishable.

A025

THE INFLUENCE OF MAGNETIC ORDERING ON THE PHYSICAL PROPERTIES OF CuFeS$_2$

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The electron energy structure of chalcopyrite CuFeS$_2$ has been calculated using the modified LAPW+lo-method with the code WIEN2k. It was shown that the splitting of d-states of Fe with different spin directions (up and down) taking into account the antiferromagnetic ordering in the layers (001) results in the appearing of the forbidden band with the calculated value near to the experimental one. This leads to the transition of this crystal CuFeS$_2$ from metallic to semiconductor state.

A026

THE MACRO- AND CRYSTALLOGRAPHIC STRUCTURE OF Li-Ti-Zn-FERRITES PREPARED WITH BALL-MILLING PROCEDURE

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The samples of Li-Ti-Zn-ferrites sintered with use of double ball-milling procedure have been investigated with X-ray diffraction, X-ray radiography, and Barkhausen noise methods. The average angles of disorientation of domains and their sizes as well as the tension in them were determined. By comparing of X-ray diffraction data received with the method θ-2θ and by the rocking curve the dimensions of the coherent-scattering regions in two perpendicular directions were found. The coherent-scattering region and the amplitude of Barkhausen noise significantly diminish with increase of the time of ball-milling.

A027

MECHANOCHEMICAL PRODUCTION OF THE PREPARATIONS MADE OF RICE HUSK

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Preparations made of rice husk might be used as biologically active additives in animal husbandry. However, rice husk is characterized by low digestibility. That is why, we focus on the experimental study of the mechanochemical reactions between silicon dioxide from rice husk and chelates; the reactions results the formation of the soluble forms of silicon. By studying the kinetics of the solubilization of the model "silicon dioxide - pyrocatechol" systems, the mechanism of the reaction of polyphenols with silicon dioxide was suggested. The mechanical treatment of pyrocatechol and natural cathehins with amorphous silicon dioxide from rice husk leads to an increase in the solubulization rate. This increase is due to the formation of chelate complexes. The preparations based on rice husk and catechins were tested and showed beneficial effects.

A028

THE INFLUENCE OF D-GUN SPRAYING CONDITIONS ON THE STRENGTHENING AND DEFORMATION OF THE Fe-Al TYPE INTERMETALLIC COATINGS

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The mechanism of plastic deformation and work hardening of Fe-Al type coatings were analyzed, considering the conditions of metalizing stream formation during D-gun spraying. The analysis of velocity, temperature and kinetic energy of powder particles forming the coatings obtained by D-gun spraying was carried out. It was found that the velocity of Fe40Al0,05Zr at%+50ppm B powder particles with particle size 15-53µm amounts from 500 to 850 m/s, depending on combustible gases mixture ratio and it has significant influence on the coatings structure. Temperature of the particles depends on powder injection position in the ignition chamber at the moment of combustible gases mixture explosion. Moreover, the particles temperature generally does not exceed their melting point, although some of Fe-Al particles are partially melted. Presented D-gun spraying conditions affect the grain morphology in coatings structure, the level of plastic deformation and the level of coatings material cold hardening.

A029

THERMAL STABILITY OF THE Fe-Al TYPE INTERMETALLICS COATINGS OBTAINED BY D-GUN SPRAYING

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The annealing of Fe-Al coatings at 750 °C for 10 hours, in spite of local coating grain fragmentation, does not break layered structure which is typical for D-gun spraying. Moreover, it does not affect coating porosity and the quality of bonding between coating and carbon steel substrate. Additionally, the annealing at 750°C causes homogenization of chemical and phase compositions and increases the level of ordering of FeAl phase, which forms the coating matrix. The coatings thus obtained exhibit elevated level of oxygen, chemically bounded in oxides thin films, mostly Al_2O_3. Presence of oxides films increases coatings heat resistance and their hardness (from 650HV.01 to 800HV.01). Hardness rising might be also a result of FeAl phase ordering, which remains stable even during long-lasting high-temperature heat treatment. The coatings annealing at 950°C does not influence coatings porosity but causes substantial decay of layered coatings structure, visible as a fragmentation of elongated FeAl grains. What is more, the coatings contain of $(FeAl)_3O_4$ spinel phase covered by tight Al_2O_3 layer preventing oxidation and corrosion in aggressive environment. The effect of slight Al diffusion to a surface layer of the steel substrate at a few micrometers deep was observed. On the one hand, it confirms deterioration of thermal structure stability. On the other hand it affects the improvement of bonding strength between coating and substrate.

A030

CERAMIC SSZ/ZIRCONIA NANOCOMPOSITE WITH HIGH CONDUCTIVITY

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Scandia stabilized zirconia SSZ is a promising candidate for IT SOFC due to high conductivity and chemical stability. The known drawback of SSZ related to a lowering of performance due to aging of ceramics was eliminated by preparing of dense nanoceramics. The application of *green technology* - mechanochemical ceramic method to synthesis of nanopowders for preparation of SSZ solid electrolyte results to inhomogeneous material – nanocomposite. In previous ISMANAM conference we reported about preparation of SSZ material with higher parameters of mechanical strength and low-temperature conductivity relatively the best regular ceramics prepared from powders produced by DKKK, Japan. However, conducting properties at operation temperature T_o ~ 1000 K were lowered in 3 times related in part to remnants of natural impurity silica drastically blocking conductivity. The objective of our study is to prepare material with the highest conductivity by optimization of chemical composition and microstructure of composite. A cheap technical grade ZrO_2 powder was used for the synthesis of composites. This reagent was purified from Si and other impurities in 3 steps by milling in planetary mill with steel media and subsequent leaching of contaminants. In such a way nanopowder with mean crystallite size about 20 nm was obtained. The content of Si was lower of limits for determination by chemical and EDS methods, estimated content was about $\leq$10 ppm. The preparation of ceramic SSZ powders was carried out for 25 min of mechanical treatment of mixture ZrO_2, Sc_2O_3 and Y_2O_3 with sintering aid. All composites from zirconia doped with Sc and Y consisted from cubic (rhombohedral), tetragonal and monoclinic phases. It was observed the strong decrease of conductivity at T_o with increase of t-phase related with Y-doping. In the sample with low t-phase content ~5%, high conductivity was measured at T_o – better than in regular ceramics obtained in close conditions from commercial powder $Zr_{0.89}Sc_{0.1}Ce_{0.01}O_{1.95}$. The best conductivity was achieved in material with relative density 0.99 after sintering at 1673 K, 1 min. Drastic increase of density from 0.94 to 0.99 and conductivity in one order after increase of sintering temperature from 1633 to 1673 K is related in part with annealing of defects like ZrO^{2+} and ZrO appeared in ZrO_2 in a result of mechanical treatment. The bands of these states were firstly observed in IR spectra. In nanocomposites $Sc11Zr/xZrO_2$ with “core-shell” microstructure, prepared from preliminary synthesized by burning SSZ matrix, structure, morphology as well as conducting properties were studied in compositions with x = 0, 0.03, 0.06, 0.09, 0.12. The mean grain size of ceramic matrix with cubic symmetry was about 800 nm, the size of embedded m-grains at room temperature - about 20 nm. The dependence of conductivity on x will be discussed in terms of interpenetrating structure concerning of mechanical strains around monoclinic nanograins in cubic matrix. Mechanochemical approach is very promising technique for the design of nanomaterials and composites with different architecture for various applications. This work is supported by RFBR, grant 09-03-364.

A035

DEVELOPMENT OF CATHODES ($La_{1-x}Sr_xMnO_{3\pm\delta}$) FOR SOLID OXIDE FUEL CELLS BY MECHANOSYNTHESIS

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Nanocrystalline powders belonging to the $La_{1-x}Sr_xMnO_{3\pm\delta}$ system (x=0, 0.25, 0.5 and 0.75) with a perovskite structure have been synthesized using a mechanochemical method. Monophase powder oxides were obtained at room temperature after one hour using a planetary ball milling equipment. XRD, ED and TEM results showed that all samples presented pseudocubic perovskite structure with a very small diffraction domain. The powder samples were conformed and sintered at 1100°C in air. After this treatment the oxides were better crystallized and showed the same rombohedrical symmetry (R_{-3c} space group 167). X-ray diffraction data verified the lattice parameter evolution due to the La substitution by Sr. Mechanochemical method is a very simple and economic alternative to synthesize electrodes for solid oxide fuel cells (SOFC).

A036

MECHANOCHEMICAL AND CATALYTIC HYDRODECHLORIN OF POLYCHLORINATED AROMATIC COMPOUNDS

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The catalyzed hydrodechlorination of aryl chlorides has been studied extensively as a potential process for nonthermal removal of persistent organic pollutants (POPs). Such dehalogenation typically proceeds in solution, via reactions with dihydrogen or various hydrogen donors (hydrogen transfer reactions), and in the presence Pd catalysts. However this method has some limitations. The mechanochemical reaction could be valuable for example in the decontamination of chloroorganic contaminated soil, the reactions are environmentally safe, as they are could be performed in closed vessels under controlled condition without the use poisonous, solvents and diffusible hydrogen gas.

The object of this study is to develop effective method for degradation high toxic POPs by using combination of mechanochemical and catalytic reaction permitting to carry out hydrodechlorination under mild reaction conditions without solution.

Catalytic properties of the samples were investigated in the reactions of the liquid phase hydrodechlorination and mechanochemical hydrodechlorination reaction of hexaclorobenzene. Monometallic and bimetallic supported catalysts, which contain Pd, Pd-Ni were prepared by precipitation of metals from their solution with following low-temperature reduction by $NaBH_4$.. As support was used carbonaceous material Sibunit. Catalysts have been characterized using methods of transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). As hydrogen donor was used sodium borohydride. The mechanochemical hydrodechlorination were performed by continuous grinding of reactant in planetary ball-mill using an agate bowl (100 ml) and 20 agate balls (10 mm diameter).

It was shown that Pd/C and Pd-Ni/C catalyzed mechanochemical hydrodechlorination of solid hexachlorobenzene with sodium borohydride allow carrying out effective dechlorination at ambient temperature. The presence of NaOH and mml amounts water (introduced in form sodium phosphate heptahydrate) lead to increasing of hydrodechlorination degree.

The authors gratefully acknowledge the Russian Foundation for Basic Research (№10-03-00372-a) for their financial support.

A037

SYNTHESIS OF ZnSe BY A MECHANICALLY-INDUCED SELF-SUSTAINING REACTION: A CASE STUDY FOR THE IGNITION TIME DEPENDENCE ON MILLING PARAMETERS

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Mechanically-induced self-sustaining reaction (MSR) compared to other mechanochemical processes has the advantage of ignition time, which can be measured by detecting the abrupt pressure increase inside the vial. Ignition is a key moment that corresponds to a critical state of reactants reached when the mill provided the necessary energy to produce MSR. Ignition time variation with process conditions reflects the mechanical dose rates of mills and allows the comparison of milling equipment efficiencies. The formation of ZnSe via an MSR process was chosen as model to study the influence of milling parameters on ignition time. Only size reduction and mixing of the Zn/Se mixture without product formation was observed during the induction period and, therefore, all the mechanical energy provided by the planetary mill was used exclusively in the activation of reactants.

A039

DEVELOPMENT OF $Ti_XTa_{1-x}C_yN_{1-Y}$-BASED CERMETS VIA A MECHANICALLY INDUCED SELF-SUSTAINING REACTION

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Ti(C,N)-based cermets have replaced cemented carbides in cutting tools due to better mechanical properties and chemical stability at high temperature. It is accepted that the use of complex metal transition carbonitrides as raw materials allows controlling the ceramic phase composition and microstructure and modulating and improving the final properties. $Ti_xTa_{1-x}C_yN_{1-y}$-based cermets with Co as binder phase were developed via a mechanically-induced self-sustaining reaction by two different methodologies. After sintering, XRD patterns showed in both cases a monophasic $Ti_xTa_{1-x}C_yN_{1-y}$ ceramic phase and an intermetallic $(Ti_xTa_{1-x})Co_2$ binder phase. However, the cermets microstructure differed; while in one case ceramic particles showed a core-rim structure, in the other case cermets presented a microstructure characterized by the coalescence of ceramic particles.

A040

MECHANOCHEMICAL SYNTHESIS OF ULTRAFINE LITHIUM GAMMA-MONOALUMINATE

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Lithium gamma-monoaluminate with the specific surface area from 10 to 20 m^2/g finds application for obtaining matrix electrolyte of molten carbonate fuel cells. The known ceramic and sol-gel synthesis methods have a number of essential shortcomings preventing their wide application. Because of this, development of new, technologically simple and ecologically safe methods of the synthesis of ultrafine lithium gamma-monoaluminate is undoubtedly interesting and urgent. Such a method may be implemented on the basis of soft mechanochemical synthesis. To develop the mechanochemical synthesis of lithium gamma-monoaluminate, we studied the effect of the conditions of mechanical activation of crystalline aluminium trihydroxide (or its mixture with lithium carbonate) and subsequent thermal treatment on the phase composition, specific surface area and particle size of the resulting lithium gamma-monoaluminate. Activation was performed in planetary activators developed at the ISSCM SB RAS: AGO-2, APF and AGO-3. Activation was carried out in steel cylinders with steel balls 3 to 12 mm in diameter. Activation time was varied from 3 to 10 minutes. Thermal treatment of mechanically activated solid phase was performed in the air within temperature range 650 to 900^{o}C. To study the products formed in the mechanochemical synthesis, we used XRD, TG and DSC, electron microscopy. The structural and morphological characterization of the synthesized lithium gamma-monoaluminate was made with the help of XRD, measurement of specific surface and particle size distribution. It was demonstrated that the mechanical activation of the mixture involves not only dispersion of the initial reagents and their mixing but also partial amorphization of the reagents, as well as the formation of carbonate form of double aluminium and lithium hydroxide. Subsequent thermal treatment at temperatures above 650^o leads to the formation of lithium gamma-monoaluminate. Optimal conditions for the synthesis of single-phase lithium gamma-monoaluminate were determined. It was shown that the specific surface of lithium gamma-monoaluminate depends on the process conditions and can reach 20 m^2/g. The data of particle size analysis provide evidence that the submicrometer-sized particles of lithium gamma-monoaluminate form aggregates of micron size.

The proposed mechanochemical technology of obtaining ultrafine lithium gamma-monoaluminate is based on using the most readily available and cheap compounds of lithium and aluminium, is almost waste-free and simple in implementation.

The investigation was carried out under the financial support from the Integration project SB RAS No. 29 and project of the programme of the Division of Chemistry and Materials Science of RAS No. 5.7.8.

A041

ELECTROCHEMICAL PROPERTIES OF Fe+Fe_3C COMPOSITES, Fe_3C AND Fe_5SiC OBTAINED BY MECHANICAL ALLOYING

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Regularities of the electrochemical behavior of Fe+Fe_3C nanocomposites (40 nm) in a concentration range of Fe_3C from 9 to 92 wt %, individual Fe_3C and Fe_5SiC as models of nonmetallic inclusions in carbon steels and siliceous cast irons are studied. The most significant factor of the corrosion behavior of Fe+Fe_3C composites is the content of Fe_3C, which is characterized by a higher potential of dissolution. With an increase in the Fe_3C content, the pitting resistance increases, and the concentration range of chlorides where pit formation is possible narrows. Fe_3C and Fe_5SiC specimens are highly active in the cathodic evolution of hydrogen in acidic environments, especially when its reticular structure is formed.

A042

MECHANOSYNTHESIS OF NANOCOMPOSITES (VC/TiC/NbC) – Fe IN LIQUID ORGANIC MEDIA

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At present development both wear- and corrosion-resistant alloys is an urgent problem. In this paper bulk Fe-NbC, Fe-TiC, Fe-VC from mixtures of Fe and V, Ti, Nb of various concentrations have been obtained in the liquid hydrocarbons medium by mechanosynthesis, followed by dynamic compaction. Structural-phase composition and morphology of the obtained multicomponent nanocrystalline powders and pressed samples have been investigated. It has been shown that mechanosynthesis in the liquid organic media in contrast to dry mechanical alloying allows obtaining high degree dispersion carbide phases with homogeneously distribution over the sample volume. It provides high microhardness of the obtained nanocomposites compared to conventional alloys. Improved corrosion resistance was been observed in the nanocomposites in neutral environments.

A043

MECHANOCHEMICAL SYNTHESIS OF NANOCRYSTALLINE SOLID FLUORIDES

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Only few papers exist on mechanical activation and/or mechanochemical reactions of solid fluorides so far. The present contribution gives an overview about mechanochemical reactions between solid fluorides performed in our lab and published recently. For example, mixtures of powders of NaF together with AlF_3 were mechanically treated by high-energy ball milling using a planetary mill. Dependent on the molar ratio of the educts cryolite (Na_3AlF_6) and/or chiolite ($Na_5Al_3F_{14}$) are obtained as reaction products. As long as NH_4F is supplied as fluorinating agent for diverse fluorine-free aluminium compounds, the formation of crystalline $(NH_4)_3AlF_6$ can be observed. Also, we succeeded in the mechanochemical synthesis of aluminium hydroxide fluoride samples with pyrochlore structure. Moreover, the distinct influence of the gaseous atmosphere on the product composition could be addressed. Structural changes were followed by ^{19}F and ^{27}Al MAS NMR and X-ray diffraction.

A044

MECHANOCHEMICALLY ASSISTED EXTRACTION OF NUTRITIOUS COMPONENTS FROM CELLULAR BIORENEWABLE MATERIALS

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This report presents description of mechanochemical and mechanoenzymatic processes that increase effectiveness of extraction of nutritious components from bio-renewable raw materials. Mechanical milling of the mixture of plant raw material and enzymes destroys the initial structure of cell walls. The concentration of defects in the biopolymers comprising the cell walls increases, while enzymes remain incorporated in the cell walls. The products of mechanochemical treatment dissolve in water yielding solution of low molecular weight polysaccharides, which can be used as components of functional nutrition and can be digested by microorganisms used in nutrition industry, e.g. in the biotechnology of alcohols.

Mechanochemical reactions with specially selected food acids, alkalis and saccharides, result in formation of soluble biologically active substances. The powder products of mechanochemical treatment contain biologically active substances in bioavailable form and can be used as components of functional nutrition

So, the application of mechanochemically assisted extraction of plant raw materials allows enhancing of the yield of biologically active and nutritious substances. In the case of unstable substances, their extraction yields can be increased by one order of magnitude. The selectivity of extraction can be also enhanced and qualitative composition of the extractable substances can be improved due to formation of water soluble components in mechanochemical reactions.

Mechanochemical approach to manufacture of BAS preparations allowed proposing of new powder and solid-state techniques. In many cases, mechanical treatment of the powder mixture of biogenic raw material and reactants allows transform of the different forms of extractable substance into one that is more soluble in a proper extractant.

Eventually, mechanochemical treatment increases the yield of the extractable substance and selectivity of extraction and opens up opportunities for using new kinds of raw material.

This approach turned out to be especially effective in cases when bioassimilable form concentration in the powder produced by mechanical treatment is sufficiently high and no additional concentration is required. Exclusion of a number of stages involving liquid phases and the stage of solid product isolation of the makes the food technology simpler and decreases concomitant expenses. The absence of liquid phases in the processing is very important and helps to prevent oxidation of unstable food components and improve the environmental safety of food manufacture.

Mechanically activated enzymatic hydrolysis may be used for obtaining mannanooligosaccharide components of functional nutrition and forage. The first procedure of mechanoenzymatic process is mechanical treatment; it provides supramolecular disordering of the cell wall polymers and increase of the β-glucan reactivity; the second stage – enzymatic hydrolysis – ensures efficient hydrolysis of glucans and leads to increase in the availability of mannanooligosaccharides

A045

MECHANOCHEMICAL SYNTHESIS OF THE LITHIUM-ALUMINIUM ANIONIC CLAYS

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The layer double hydroxides (LDHs or the anionic clays) have become the focus of intense activity in both scientific research and industrial application. LDHs consist of univalent, divalent and trivalent metal cations of a brucite-like structure, with anions and water molecules located between layers. The univalent cation is always only Lithium. The LDH has numerous applications but the synthetic process and the structure of Li-Al LDH is not clear. This work compares the synthesis of Li-Al (Cl)-LDH by a mechanochemical route (utilizing a shaker, agate bolls, 325 rpm for 24-48 hours) with the products from synthesis by the co-precipitation method with different ratios of Li/Al. For analysis we have used titration procedures, ICP-AES and thermal analyses, XRD powder data, and FTIR spectra. Additionally the "structure memory" effect which uses a heating-rehydration treatment was applied. The results of these data and recommended conclusions are discussed.

A046

THE VARIABLE THERMOELECTRIC EFFECT IN MAGNETIC VISCOSITY ALLOY Fe86Mn13C

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In given work the thermal electromotive force was detected at various points in the shock-deformed samples of alloy Fe86Mn13C.The electromotive force was established that as a result of long mechanical loading on an austenitic alloy Fe86Mn13C. In its structure, besides known phases of deformation martensite, Frank-Kasper structures can be formed. The variable temperature dependence of thermal electromotive force in samples of alloy Fe86Mn13C has been detected. It has been noticed that at heating of the sample, its property are identical to properties of the thermocouple. If the sample has not been subject to shock strain value the contact potential difference effect was absent It is determined that in Fe-Mn and Fe-Mn-C alloys there is the complicated magnetic order similar to an order in spin glass, which is installed thanks to coexistence of interacting antiferromagnetic and ferromagnetic phases. Structural studies of alloy Fe86Mn13C may indicate such states and give the answer to the cause of magnetic viscosity. Electronic structure calculations for nanocrystalline Fe87Mn13, by the scattered waves method, were showed the presence of energy gaps in the spectra of the electron density of states of nanocrystalline having a structure of the Frank-Kasper. They are most easily formed from the nonequilibrium state in metallic alloys Sign thermo electromotive force may vary depending on the temperature. The reason for its appearance is connected with the contact potential difference at the interface of two phases: the antiferromagnetic austenite and ferromagnetic martensite deformation. The nature of the appearance of variable thermoelectric effect can be explained from the standpoint of coexistence in the samples of the inhomogeneous crystal and magnetic structures. The effect of magnetic viscosity in samples of alloy Fe86Mn13C and its change under the influence of long-term impact of mechanical loading was detected.

A047

THE ACTIVATION BY LIQUID – PHASE DISPERSION

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Soldered joints with composite juncture were realized using the liquid-phase dispersion which was determined by a number of physical (mechanicochemical, thermodynamical, thermo-deformational) and kinetic (thermo-mechanical) criteria. The most activated criterion turned out to be the processes of thermo-deformational ones because of the augmentation of density of spot-type vacancies and line dislocations which arose in the surface layers of the metallic details by infrasonic induction via the molten solder. The experiments justified the capacity of the activation of dispersion of copper plate through all (1.0 mm) thickness by micron- and nano-dimensional grains in the matrix of solder contributing growing of strength and the temperature of unsoldering of soldered joints.

A048

MECHANOCHEMICAL SYNTHESIS OF ALKALINE NIOBATES AND TANTALATES: UNDERSTANDING REACTION MECHANISMS

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Alkaline niobates and tantalates constitute a technologically important group of materials and show a continuous interest due to their wide range of applicability. As an alternative to the conventional solid-state synthesis method, the mechanochemical approach has been applied to synthesize a variety of compositions among these materials. This paper aims to provide an in-depth review of the mechanochemical synthesis of alkaline niobates and tantalates, stressing the current understanding of the reaction mechanisms. After the mechanochemical synthesis of the model $NaNbO_3$ system will be presented, the kinetics of the Na_2CO_3–M_2O_5 (M = V, Nb, Ta) reactions will be further discussed. Finally, the key role of the mechanochemical activation in view of obtaining $(K,Na,Li)(Nb,Ta)O_3$ and $KTaO_3$ with improved piezoelectric and dielectric properties, respectively, will be demonstrated.

A049

THE INFLUENCE OF MECHANOACTIVATION ON A BIOLOGICAL ACTIVITY OF HUMIC ACIDS FROM PEAT

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Mechanochemical activation of peat allows improvement the efficiency of humic acids extraction and can cause the increase in availability of their separate components and parts of molecules, including micro- and macroelements which are used as sources of nutrition and energy by a microbe cell. It was shown the addition of humic acids isolated from mechanoactivated peat, in petropolluted soil increases the number of hydrocarbon-oxidizing microorganisms in 6-15 times and their enzymatic activity in 3-6 times. Herewith, processes of biodegradation of petropollution in soil proceed in 2-3 times more intensively and additives of humic acids into petropolluted soil reduce the quantity of residual oil in 40 %. The changes in content of n-alkanes contamination in the process of microbiological degradation were defined.

A050

LOW-TEMPERATURE SYNTHESIS OF ALUMINUM NITRIDE

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Direct interaction between aluminum and nitrogen requires high temperatures (> 1500C) due to strong oxide film covering the surface of the metal. Attempted breakage of that film by mechanical action aimed at facilitating solid-gas reaction fails since the protective film immediately restored on exposure the treated metal to an atmosphere with even negligible amount of oxygen or nitrogen. Mechanochemical reaction resulted in formation of organic coating on the fresh metal surface has been carried out simultaneously with film breakage. Subsequent heating of thus prepared precursor in the flow of nitrogen led to evaporation of the coating followed by nitride synthesis, the latter being completed at little more than 900C. The product represents a sponge which can be easily comminuted in a mortar or in a mill to give a powder that has been sintered to dense ceramics with high thermal conductivity.

A051

THE CHANGE OF BINDING ABILITY OF HUMIC ACIDS WITH PESTICIDES AT MECHANOACTIVATION OF CAUSTOBIOLITHS

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The use of humic acids as detoxicants at recultivation of the polluted environments is required carrying out of the directed modification of structure and properties of humic preparations. One of methods for the decision of this problem is mechanical activation of solid caustobioliths with addition of an alkaline reagent. The average molecular weight humic preparations, extracted from mechanoactivated samples, decreases on 25 - 30 %. The quantities of functional groups containing oxygen which take part in the interaction with pesticides and also chelating groups increase in the structure of humic acids. Modified humic substances are associated with pesticides more efficiently forming strong complexes and weakening their toxicity.

A052

AN INVESTIGATION ON MECHANOCHEMICAL ACTIVATION OF SOLIDS AND ITS APPLICATION TO MATERIAL PROCESSING

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It is known that high-energy ball milling a material causes mechanochemical activation on it, and the activation appears significantly in the prolonged milling time periods. This activation is due to creation of new surface produced caused on the milled material. Thus, the activation starts in the stage of a short milling time period, and it is accelerated in the prolonged milling stage. This activation is known to be recognized in changing its crystal structure from crystalline to amorphous phase, one crystalline to another, which is called as polymorphic transformation. In addition to that, the activation could be used for synthesizing a material from multi-components of staring samples without heating. This phenomenon is also known well as mechanochemical reaction, and the obtained product has often shown different property from that of the staring samples, as shown below:

1) Intensification of dissolution and leaching processes.
2) Increase in the rate of decomposition and synthesis.
3) Activation of catalytic function.
4) Improvement of existing technological processes such as sintering.
5) Preparation of substances with new properties.
6) Control of mineral properties in the field of ore dressing

We have attempted this mechanochemical activation for several materials processing, such as direct synthesis of a material, separation of formed products from the milled samples by washing with water/solubent after dry milling starting samples such as minerals and waste materials. We have created a novel process for generating pure hydrogen and syngas from biomass and polymer resins such as polyvinyl chloride (PVC) and poly-ethylene (PE) by its heating after the milling under dry condition. All the same, the mechanochemical activation is a important key to stimulate the following operations.

A053

FUTURISTIC ENERGY CREATED FROM CELLULOSE-BASED BIOMASS BY ITS THERMAL DECOMPOSITION WITH AN AID OF MECHANOCHEMICAL TREATMENT

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There has been a growing demand for developing processes to generate H_2 for energy resources and feed gas for fuel cells. We have proposed a novel process for generating pure H_2 from biomass (waste wood, cellulose based materials) through its mechano-chemical treatment with additives such as $Ca(OH)_2$ and $Ni(OH)_2$, followed by heating the milled sample at around 400 °C. The starting sample was a mixture of biomass, $Ca(OH)_2$ and $Ni(OH)_2$, and they were subjected to milling by a planetary mill under room temperature. The milled mixture was heated by an electric furnace under Ar gas atmosphere. The gasses generated from the furnace were characterized by different methods, confirming pure H_2. Hydrogen at high purity over 90% can be obtained with different temperature ranges where the gas amount varies depending on the temperature. The reaction during the heating is shown as below.

$$C_6(H_2O)_5 + 6Ca(OH)_2 + 0.5Ni(OH)_2 = 11.5H_2 + 0.5Ni + 6CaCO_3 \quad (1)$$

$Ni(OH)_2$ can be easily reduced into metal nickel by hydrogen, and it plays a big role to generate hydrogen. $Ca(OH)_2$ performs to capture carbon (C) and oxygen (O) in the molecule of biomass to form $CaCO_3$ in the heating operation. When $Ca(OH)_2$ added to the biomass sample is increased up to 14 moles, hydrogen purity reaches over 90%. All the same, milling the starting samples is very important to intimate the contact among them, and the effect can be realized to form $CaCO_3$ with generating high concentration of H_2 in the heating stage. Thus, this serial operation of grinding and heating the mixture would be useful for generating high purity H_2 from biomass which is one of the renewable energy sources in the future.

A054

SOLID-LIQUID MECHANICAL SYNTHESIS OF NANOCOMPOSITES BASED ON HYDRIDE/CARBIDE-FORMING METALS

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The evolution of metal-organic systems under high-energy ball milling is investigated. We used the hydride/carbide-forming titanium and hydride-forming magnesium as metals, and toluene and n-heptane as organic liquids. It is established that due to destruction of the organic molecules the titanium hydride and carbide are formed during milling. The magnesium hydride formation and carbon saturation in the solid phase are observed in the Mg-toluene system. The content of the magnesium hydride after 22 h of milling is 11 wt.%. These Mg-C-H nanocomposites have high hydrogen storage ability at low hydrogen pressure. The processing of Mg with n-heptane results in a powder particle/grain refinement only. Support for this work was provided by RFBR (grant 10-08-90419-Ukr_a).

A056

INITIAL STAGE AND MECHANISMS OF MECHANICAL SYNTHESIS IN EXOTERMIC SYSTEM Ti-C

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A nanocrystalline titanium carbide is obtained by mechanochemical synthesis (MS) in a planetary ball mill from a powder mixture Ti(50)C(50) of titanium and graphite. Either gradual or abrupt reaction occurs depending on the power intensity of the mill. Critical power intensity for the transition from the gradual to abrupt kinetics is found. It is shown that the structural state of Ti-C system directly before beginning of the reaction is identical irrespective of the subsequent kinetics of MS. Moreover, the dozes of mechanical energy necessary for the beginning of both gradual and abrupt reactions are equal and do not depend on the power intensity of the mill. The mechanism in which deformation-induced interdiffusion is responsible for beginning of MS, and reaction heat released is motive force of ignition of self-propagating reaction is considered.

A058

RECENT ADVANCES IN MECHANOCHEMICAL SYNTHESIS OF OXIDE POWDERS WITH 1D AND 2D MORPHOLOGY

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Mechanochemical synthesis of oxide nanopowders is currently widely studied. However, in some cases, the potential of mechanochemical synthesis starting from reactive precursors can be successfully enhanced by using the careful washing treatment of the as-prepared mixture, or by subsequent annealing at temperatures in excess of the melting point of the new-formed salt matrix. In this work, we present the synthesis of oxide nanostructures such as TiO_2, VO_2, Al_2O_3, and $Na_2Ti_6O_{13}$ with well-developed 1D and 2D morphology prepared from their reactive precursors. Transmission electron microscopy (TEM) was used to show the 1D and 2D morphology of powders.

Acknowledgement: This work was supported by Agency of the Ministry of Education of the Slovak Republic for the Structural Funds of the EU, Operational Programme Research and Development, Project Codes 26240120011 and 26220120014, and by VEGA grants 2/0160/10 and 2/0020/11. The authors wish to thank to Kadaň Ltd. Slovakia.

A059

TOPOLOGICAL MODELS FOR SELF-ADAPTIVE NETWORK CLUSTERS IN CHALCOGENIDE GLASSY-LIKE ALLOYS

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Chalcogenide compounds prepared by mechanical alloying from a melt using vibration-rotation mixing are known to possess unique ability to form glassy-like networks distinguished by full saturation of interatomic bonding. These alloys attain three distinct phases dependently on relation between numbers of bonds and mechanical Lagrangian constrains per atom: floppy (under-constrained), elastically rigid but unstressed (optimally-constrained) and enthalpically-stressed rigid (over-constrained). Percolation transition from elastically floppy to stressed-rigid networks predicted to be solitary, but it split into two points by accepting that bonds reveal a tendency to self-adaptability. We have presented computational modelling approach based on *ab initio* quantum mechanical calculations to describe self-adaptive network-forming structural clusters in chalcogenide glassy alloys.

A060

ROLE OF FREE-VOLUME COORDINATION DEFECTS IN EQUILIBRIUM-RELAXATION PROCESSES IN MIXED ARSENIC-ANTIMONY-SULPHUR GLASSY ALLOYS

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Structural evolution caused by defect relaxation towards thermodynamic equilibrium were studied using optical and positron annihilation spectroscopy in melt-quenched glassy alloys of quasi-binary arsenic-antimony sulphides subjected additionally to radiation treatment. Positron lifetimes determined in low-measurement statistics were shown to be in good agreement with observed decaying kinetics of optical darkening. In both cases, the relaxation constants tended towards two days only slightly decreasing with antimony sulphide content. This result testifies in a favour of the same nature of free-volume coordination defects responsible for both changes. The microstructural mechanisms of corresponding defect formation processes ascribed to direct destruction of heteroatomic covalent bonds as well as heteropolar-homopolar bond switching are discussed in details.

A061

INFLUENCE OF HIGH- ENERGY BALL MILLING OF TUNGSTEN OXIDE WO_3 PRECURSOR ON THE TUNGSTEN NITRIDE W_2N PERFORMANCE IN SUPERCAPACITORS

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Considerable efforts are devoted today to the development of inorganic electrode materials for supercapacitors with low cost and high capacitance. We have recently established that tungsten nitride W_2N is one of the promising materials. Pseudomorphic reduction of tungsten oxide WO_3 in Ammonia gas is a convenient way to prepare tungsten nitride. In this work, we are evaluating how the high- energy ball milling of WO_3 precursor in the planetary ball mill affects the structural characteristics and electrochemical performance of W_2N. Electrochemical properties of tungsten nitride have been evaluated by measuring the potential window, the specific capacitance and the stability of the electrodes in aqueous solutions.

A062

THE EFFECT OF TEMPERATURE DURING MECHANICAL TREATMENT ON CONVERSION OF ORGANIC PART OF BROWN COAL

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Practically all kinds of chemical-technological processing of coals are connected with their dispersion. Local rise of temperature in the impact zone and mechanical tensions in coal particles arising at their fracture are those factors under the influence of which certain chemical conversions occur. One can suppose that mechanochemical treatment of coal at elevated temperatures will promote the obtaining of coal capable to more complete conversion at further processing, in particular in such a process as liquefaction. The aim of the present investigation was to study mechanochemical conversions of organic part of brown coal at temperatures ranging from 20 to 200 ^oC. The experiments on mechanochemical treatment of the coal were carried out using installation AGO-2. Steel balls 8 mm in diameter were used as grinding bodies, centrifugal acceleration of grinding bodies was 600 m/s^2 and time of mechanical treatment was 10 minutes. Brown coal recovered from Barandatskoye coalfield, Kuzbass coal basin, was used as an object under study. Mechanical treatment was accompanied by the release of gaseous products. Nitrogen, methane and ethane were determined in a gaseous phase. Great amount of carbon dioxide released during mechanical treatment of the coal (18 vol. % – mechanical treatment at 200 ^oC). The release of gaseous hydrocarbons at mechanical treatment evidenced partial destruction of organic part of the coal.

Due to rise of temperature at mechanical treatment of the coal from 20 to 160 ^oC the yield of bitumoid increased. The fact of the increased yield of bitumoids from mechanically treated coal is universally recognized and related both to reduced sizes of coal particles (opening of inner pores) and components destruction. At the same time mechanical treatment of the coal carried out at 200 ^oC results in decreased yield of bitumoid. It is evident that at this temperature deeper destruction of organic constituent of the coal occurs to form methane and ethane causing decreased yield of bitumoid. The content of oil fraction in liquid products of mechanically treated coal is lower as compared with initial coal. In the temperature range of mechanical treatment 20 ÷80 ^oC the content of oil fraction decreases from 50.1 % to 43 wt %. The yields of oil fraction at mechanical treatment carried out 160 and 200 ^oC are nearly the same. With the rise of temperature of mechanical treatment the amount of resins and asphaltenes in liquid products increases as compared with initial coal. The data obtained evidence that at elevated temperatures of mechanical treatment hydrocarbons of oil fraction are mainly subjected to destruction. The carried out investigations demonstrated that with rise of temperature at mechanical treatment of the coal from 20 to 160 ^oC the yield of bitumoid increases and noticeable destruction of hydrocarbons begins at the temperature of 200 ^oC.

A063

THE EFFECT OF MECHANICAL TREATMENT INTENSITY ON COMPONENT COMPOSITION OF HIGHLY PARAFFINIC CRUDE

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Partial destruction of crude hydrocarbons is known to occur during mechanochemical treatment however the effect of such treatment intensity on the conversion of hydrocarbons in highly paraffinic crude has not been studied yet. It was the aim of the present investigation. Crudes recovered from Stolbovoye (content of paraffin waxes 6.9 wt. %) and Zuunbayan (content of paraffin waxes 16 wt. %) deposits were used as the objects under study. Mechanochemical treatment of crudes was carried out using installation AGO-2M. Steel balls 8 mm in diameter were used as grinding bodies. The intensity of mechanical treatment was specified by rotational speed of the reactor; the experiments were carried out at grinding body acceleration of 300, 600 and 1000 m/s^2 and time of mechanical treatment was 10 minutes. In all experiments one fixed no formation of gaseous hydrocarbons. The content of asphaltenes in crude recovered from Stolbovoye deposit increased with increase in the intensity of mechanical treatment (in the initial crude it was 1.6 and in mechanically treated at acceleration of 1000 m/s^2 - 2.4 wt. %). The content of resins decreased (in the initial crude it was 9.3 and in mechanically treated at acceleration of 600 m/s^2 – 8.5 wt. %). The content of oils in crude from Stolbovoye deposit remained practically unchanged being independent on the intensity of mechanical treatment. One observed small increase in asphaltene content in crude from Zuunbayan deposit (in the initial crude it was 0.22 and in mechanically treated at acceleration of 600 m/s^2 – 0.88 wt. %) and decreased content of resins (in the initial crude it was 14.67 and in mechanically treated at acceleration of 600 m/s^2 – 8.3 wt. %). With the increase in the intensity of mechanical treatment the content of oils in Zuunbayan crude increased insignificantly (in the initial crude it was 85.11 and in mechanically treated at acceleration of 1000 m/s^2.- 90.2 wt. %). Element analysis testified that after mechanical treatment the content of sulfur, carbon and hydrogen in both crudes decreased insignificantly. With the increase in the intensity of mechanical treatment the content of paraffin waxes in crude from Stolbovoye deposit decreased. In Zuunbayan crude at acceleration of 300 m/s^2 the content of waxes in mechanically treated crude corresponded to their content in the initial crude. At the intensity increase up to 600 m/s^2 the content of waxes in mechanically treated crude decreased, whereas at further increase (1000 m/s^2) one observed the increase in their content. Based on the investigations it was determined that mechanochemical treatment of highly paraffinic crudes can be accompanied with both hydrocarbon destruction and condensation.

A064

NEW MECHANOCHEMICAL AND MICROWAVE METHODS FOR SYNTHESIS OF PLATINUM GROUP METAL BETA-DIKETONATES AS MOCVD PRECURSORS

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Nanostructural film materials on the base of platinum group metals are widely used in space instrument engineering, electronics, optics, catalysis, electrochemistry, jeweller's industry etc. MOCVD (Metal Organic Chemical Vapor Deposition) technique is one of the modern methods for forming metal and composite layers. The chemistry of used volatile compounds plays a key role in MOCVD processes, so precursors must be volatile, have good thermostability and high yield at synthesis. In a greater extent it concerns platinum group metals beta-diketonates in view of high cost of metals. As a rule, there are no universal techniques for preparing this class of volatile compounds, and product yields presented in literature are no more 20% in most cases. Test experiments of obtaining Ir(III), Ru(III), Rh(III) acetylacetonates were carried out with using mechanochemical combined microwave methods. Metal chlorides, potassium acetylacetonate and potassium bicarbonate were used as initial reagents. Reactions were realized both in solid state and solutions. Yields were varied up to 20%. The purity of synthesized compounds was controlled by the element analysis, IR- and NMR-spectroscopy.

A065

Fe-BASED AMORPHOUS AND NANOCRYSTALLINE ALLOYS PROCESSED BY MECHANICAL ALLOYING

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Nowadays mechanical alloying (MA) and milling (MM) are widely recognized as techniques allowing fabrication of powder alloys. Originally developed for the production of oxide dispersion strengthened nickel based alloys, now this method is used for synthesis of many alloys showing equilibrium or non-equilibrium phases, depending on thermodynamic and kinetic parameters of the process. Amorphous alloys, intermetallics, solid solutions, quasicrystals, nanostructured materials and many others can be obtained by MA or MM. This talk focuses on the Fe-based alloys synthesised by MA. The variety of the structures formed by powder milling and their characterization are presented, literature data as well as and own experimental results are discussed.

A066

DEVELOPMENT OF ENERGY APPROACH FOR ANALYSIS OF MECHNOCHEMICAL PROCESSES DYNAMICS

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In defect-free solids under the temperatures, which are significantly below melting point, molecular mobility, diffusion and reactivity are frozen by the strong crystalline field. For realization of reactivity in such conditions it is necessary to apply additional nonthermal energy. In mechanochemical reactor there are simultaneously applying of stresses, plastic deformation and relaxation of mechanical energy. In the context on “energy approach” the amount of products N, which are formed in the high power mechanochemical reactor, is the function of applied energy (dose D). The parameter of efficiency of energy using is energy yield, which is defined in integral form as $G=N/D$. The kinetics of different mechanochemical transformation are analyzed in the context of this approach and characters of dose dependences $N=f(D)$ are revealed in any limiting cases.

A069

MULTISCALE DESIGN OF CoAlO/CoAl CERMET PREPARED FROM Co-Al ALLOYED PRECURSOR

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The comprehensive study of CoAlO/CoAl porous cermet monolith prepared from Co-Al alloyed precursor through hydrothermal treatment and following calcination at 900°C was performed using most suitable techniques such as XRD, SEM, TEM, internal ^{59}Co NMR, and EDX including 2D mapping. The cermet was found to compose of metallic cores distributed in the porous oxide matrix. The cores contain both fcc Co and Co-Al alloy nanoparticles greatly increasing the cermet crushing strength and preventing Co oxidation. The interface between cores and matrix is alumina also protecting the cores from oxidation. In turn, the oxide matrix was proved to consist of spinel cobalt aluminates surrounding the cores and outer matrix part is represented by cobalt oxides. The relation between powdered alloy precursor and cermet monolith has been discussed.

A070

THE MICROSTRUCTURE AND PROPERTIES OF ZnO ACTIVATED BY BALL MILING

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A zinc oxide is well known material that finds many industrial applications. Several schemes of mechanical activation have been developed to prepare of nanosized ZnO. According to V. V. Molchanov et al. catalytic activity of ZnO powders increases after mechanochemical activation in a planetary mill. The purpose of this study is to investigate the effect of milling conditions on the microstructure, particle size and photocatalytic properties of the obtained products. As-supplied polycrystalline ZnO powder (Sigma - Aldrich, <100 nm) was subjected to mechanical treatment in air using a planetary ball mill (Fritsch – Premium line – Pulversette №7) at different milling speed from 1 to 60 min. Lowering of average grain size as a result of milling has been estimated from the broadening of x-ray lines. It is established that ball milling at lower speeds and shorter time is more suitable for better photocatalytic activity.

Acknowledgments: The study was performed with financial support of The Ministry of Education and Science of Bulgaria, The National Science Fund of Bulgaria, Contra No TK-X-1702/07.

A071

PREPARATION OF TiO_2/MoO_3 MIXED OXIDE POWDERS BY BALL MILLING

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It is well known that TiO_2 and MoO_3 are semiconductors and they find different applications. According to the phase diagram in this system there are not crystalline phases. It is interesting to verify whether coupling of both oxides will lead to modification of their properties. TiO_2 : MoO_3 in different molar ratios (95 : 5 mol %; 90 : 10 mol%, 50 : 50 mol% and 10 : 90 mol%) were subjected to intense mechanical treatment in a planetary ball mill (Fritsch – Premium line – Pulversette №7) at different milling speeds from 1 to 300 min. The obtained composites were characterized by X-ray diffraction (XRD) and UV-Vis spectroscopy. After milling a reduction of the particle size of both oxides was observed. The optical absorbance measurements were strongly affected by the MoO_3 content. All samples exhibited high photocatalytic activity against degradation of Malachite Green (MG) under UV-light irradiation.

Acknowledgments: The study was performed with financial support of The Ministry of Education and Science of Bulgaria, The National Science Fund of Bulgaria, Contra No TK-X-1718/07.

A072

INFLUENCE OF SUBSTITUTION OF TANTALUM FOR HAFNIUM ON THE ELECTRONIC STRUCTURE OF CUBIC $Hf_xTa_{1-x}C_y$ CARBIDES: *AB INITIO* BAND-STRUCTURE CALCULATIONS AND X-RAY SPECTROSCOPY STUDIES

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Transition metal carbides are of considerable interest, both from a theoretical and a technological point of view. The carbides possess unusual combination of physical and chemical properties: high hardness, corrosion stability and melting points, good electrical and thermal conductivity, superconductivity at low temperatures and plasticity at high temperatures. Tantalum and hafnium monocarbides are of particular interest because they are the highest melting point materials known so far, namely 3983 and 3928 ^{o}C for TaC_x and HfC_x, respectively. The chemical bonding in the carbides is a superposition of ionic, covalent and metallic components; therefore, an interpretation of the electronic structure of the compounds is rather difficult. To investigate the influence of substitution of tantalum atoms for hafnium atoms in the cubic (NaCl structure) $Hf_xTa_{1-x}C_y$ carbides, total and partial densities of states were calculated for HfC, $Hf_{0.5}Ta_{0.5}C$ and TaC using the *ab initio* band-structure augmented plane wave +local orbitals (APW+LO) method as incorporated in the WIEN2k code. The theoretical data reveal that a strong hybridization of the Hf(Ta) 5d- and C 2p-like states is characteristic for the $Hf_xTa_{1-x}C_y$ carbides. X-ray photoelectron spectroscopy (XPS), X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) methods were employed in the present work to verify experimentally the theoretical data for the carbides under consideration. The XPS valence-band and core-level spectra, the XES bands reflecting energy distributions of mainly the Ta 5d- and C 2p-like states as well as the XAS Ta(Hf) L_{III} edges (unoccupied Ta(Hf) d-like states) were derived and compared on a common energy scale for cubic $HfC_{0.94}$, $Hf_{0.5}Ta_{0.5}C_{0.95}$ and $TaC_{0.98}$ compounds. In the present work a rather good agreement of the experimental and theoretical results for the electronic structure of the $Hf_xTa_{1-x}C_y$ carbides was achieved. It has been established that, substitution of hafnium atoms by tantalum atoms in the $Hf_xTa_{1-x}C_y$ system reveals increasing the full width at half maximum of the XES C Kα band. When going from $TaC_{0.98}$ to $HfC_{0.94}$ through the carbide of intermediate composition, the main maximum of the XPS valence-band spectrum shifts in the direction toward the position of the Fermi level. In the above sequence of carbides the asymmetry index of the C Kα band increases significantly.

A073

MECHANOCHEMICAL SYNTHESIS OF NANOPHASE COMPOSITES IN $La_{1-x}Sr_xFeO_{3-y}$ PEROVSKITES: FORMATION OF $LaSrFeO_4$ SURFACE RICH COMPOSITES

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Mixed oxides with perovskite structure are widely used in different high-temperature applications as catalysts, cathode materials of SOFCs, membrane materials etc. Mechanochemical (MC) method is known as very promising approach for perovskite preparation. In this communication the influence of Sr containing precursor taken for MC synthesis on phase and surface composition, microstructure and reactivity of $La_{1-x}Sr_xFeO_{3-y}$ oxides is discussed. Samples of $La_{1-x}Sr_xFeO_{3-y}$ system ($0 \le x \le 1$) were prepared from La_2O_3, Fe_2O_3 and $Sr(NO_3)_2*6H_2O$ or $SrCO_3$ by powder mixture preliminary mechanic treatment following by calcination at 1100-1200 ^oC for 4 hours. Samples were named as “N-series” and “C-series”, correspondingly. Detail investigations of the surface/bulk composition, structure in both series (by using XRD, DTA, differential dissolution method, HREM) were revealed the influence of Sr precursor: different types of nanocomposites are obtained. The specialty of phase composition in N-series perovskites is in formation of supported $LaSrFeO_4$ phase on the surface of $La_{1-x}Sr_xFeO_{3-y}$ perovskites for samples $0.2 \le x \le 0.75$. Oxides of C-series are single-phase perovskites $La_{1-x}Sr_xFeO_{3-y}$ excepting samples situated in the region of morphotropic phase transition ($0.3 \le x \le 0.4$) and comprised of cubic and orthorhombic phases $La_{1-x}Sr_xFeO_{3-y}$. Comparison of reactivities of series also pointed out on influence of microstructure peculiarities obtained by using of different Sr precursor. So, studies on catalytic performances of systems are revealed that in perovskite of C-series the Sr-substitution leads to the decreasing of specific catalytic activity (SCA) value in CH_4 oxidation process. In contrary of C-series, for samples of N-series SCA value reaches its maximum on the sample with x=0.75 characterized by maximum amount of randomly situated anion vacancies and presence of supported $LaSrFeO_4$ nanocomposites on the surface.

A074

HYDRIDING PROPERTIES OF MAGNESIUM-BASED NANOCOMPOSITES

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Magnesium and magnesium-based alloys are very attractive for hydrogen storage due to high hydrogen capacity. However, relatively high stability of magnesium hydride, slow kinetics and incomplete transformation of magnesium into hydride are significant drawbacks for wide practical use of magnesium. In recent years the main tendency in improving hydriding properties of magnesium consist in fabrication of nanocrystalline magnesium-catalyst composites predominantly by means of reactive mechanical milling under hydrogen atmosphere. As a rule, these composites possess excellent kinetic characteristics of hydriding and dehydriding reactions. But some peculiarities (such as “hysteresis” phenomenon, unusual shape of kinetic curves at hydriding and very strong dependence of reaction rate on hydrogen pressure) have been revealed in reaction of hydrogen with nanocrystalline magnesium. Moreover, contrary to expectation, magnesium-based nanocomposites did not achieve a full degree of transformation into hydride especially at low temperatures.

All these peculiarities can be explained by hampered hydride nucleation in nanocrystalline magnesium. Due to very low solubility of hydrogen in magnesium the number of hydrogen atoms dissolved in nano-sized particle may be not enough for formation and growth of a critical nucleus of magnesium hydride. Some part of nano-sized particles remains unreacted because nuclei of magnesium hydride can not be formed. It leads to decrease of hydrogen capacity and to quick deceleration of the reaction, particularly at experimental conditions in the vicinity of equilibrium which clears up the apparent hysteresis phenomenon observed by many researches.
Special experiments have shown that these phenomena become more pronounced when nano-particles of magnesium are separated from each other by mechanochemical treatment with a large quantity of an inert MgO compound. It evidences that the contacts between magnesium nano-particles facilitate nucleation process owing to hydrogen diffusion from one particle to another, by all appearances.

The detected peculiarities in hyding properties of nanocrystalline magnesium should be taken into consideration at further investigation and development of nanocomposite hydrogen storage materials.

A075

MECHANICAL OSCILLATIONS AND THERMODYNAMICS OF EXTRATHIN CRYSTALLINE FILMS

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This paper presents results of phonon subsystem investigation of extra-thin film-structures, i.e. two-layered crystalline samples, using two-time dependent Green's function method. Essential mechanical properties of given system can be obtained and interpreted analytically through this method, especially the influence of boundary parameters of the film on to the changes of phonon states. Possible states of phonons are determined and energy gaps were examined and recorded and emergence of the highest activation energy was recorded under certain conditions as well. Finally, phonon contribution to the thermodynamic and superconducting properties of these highly bounded nanostructures was discussed.

A076

MONTE CARLO STUDY OF PHONON SUBSYSTEM IN ULTRATHIN CRYSTALLINE SAMPLES

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Phonon subsystem of ultrathin films is analyzed within a Monte Carlo approach in order to obtain general thermodynamic properties. Such approach is chosen to compare and check the results, mainly phonon dispersion law and internal energy of observed system, which we obtained analytically through the two-time dependent Greens functions method. Later, the goal was to determine and interpret the results concerning the thermodynamic role of phonons in the low temperature area.

A077

MECHANOCOMPOSITES WITH ACTIVE METALS FOR THE TRADITIONAL METHODS OF OXIDES REDUCTION

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Results of the structural investigation of nanocomposite powders Cu-Ti and Cu-Zr formed by mechanical activation in a planetary ball mill AGO-2 are presented. Both systems have negative mixing enthalpy and can form intermetallics and solid solutions. In spite of this fact, nanocomposite powders without chemical interaction between metals have been obtained. Despite significant widening of the Cu reflexes, no change in their positions in the XRD diffraction patterns is observed even after long-term treatment, arguing against the solid solution formation. Two-phase structure containing nanosized Ti (Zr) particles uniformly distributed in nanocrystalline Cu matrix is formed. Such mechanocomposites can serve as precursors for the following traditional methods of oxides reduction, providing improvement of the processes and their product properties.

A078

Cu/ZrO_2 COMPOSITES PREPARED BY SELF-PROPAGATING HIGH-TEMPERATURE PROCESSING OF THE MECHANICALLY PRE-ACTIVATED CuO/Cu/Zr SYSTEM

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The preparation of (Cu/ZrO_2) composites by mechanical activation of the [CuO + (Cu + Zr)] system followed by self-propagating high-temperature synthesis (SHS) has been explored. We used the combined (double) mechanical activation of the [CuO + (Cu + Zr)] system to prepare precursors for the subsequent SHS. At first, Cu and Zr metals were mechanically activated in a high-energy ball mill, forming the Cu/Zr nanocomposites. In the second step, the mixture of the nanocomposites with CuO was mechanically activated for 4 min, leading to the CuO/Cu/Zr mechanocomposites. The use of the as-prepared mechanocomposites instead of CuO/Zr ones changes a mechanism of interactions between the reactants during the SHS from the thermal explosion mode to the steady-state combustion with the burning velocity and temperature of about 2 mm/s and 1044 °C.

A079

THE PREPARATION OF MECHANOCOMPOSITES W-Me-ORGANIC SUBSTANCE AND INVESTIGATION OF THE INFLUENCE OF TYPE OF ORGANIC PLASTICIZER ON THE COMPRESSIBILITY OF THE OBTAINED MECHANOCOMPOSITES

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The work aim is to study structure and morphology of the composites formed at mechanochemical activation of the tungsten with a small content (till 10 %) of metals both interacting (Ni, Fe, Zr, Ta, Hf) with it and immiscible (Cu) with it. The influence of mechanochemical introduction of the organic plasticizers into tungsten based materials without the use of solvents to improve compactibility in decreasing the organic plasticizers' content has been studied. The influence of the type and quantity for incorporated organic plasticizer on tungsten-metal compositions' compactibility has been investigated. The work was carried out within the framework of Fundamental Research Programme of Russian Academy of Sciences "Elaboration of chemical substances attaining methods and new materials creation", project No 7.21.

A080

MECHANICAL BEHAVIOR OF MECHANICALLY ACTIVATED CARBON-QUASICRYSTAL COMPOSITE

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Quasicrystal based composite materials are of great importance, because they exhibit higher mechanical properties than those attained using conventional intermetallics. In this work, $Al_{70}Cu_{20}Fe_{15}$ icosahedral quasicrystal and mechanically activated carbon (graphite) composite materials are investigated. The mechanically activated carbon (MAC) was prepared using a high-energy planetary mill at 600 rpm in toluene medium as a process control agent, for 80 h. When MAC milled (100 rpm) with the quasicrystalline phase was dissolved into an intermetallic solid solution; low intensity milling (100 rpm) with MAC showed to conserve the quasicrystalline (QC) phase, whereas the small amount of nano crystallization B2 phase was achieved during the milling process. Mechanical behavior study of sintered samples (200 ˚C) showed an increase in the hardness of the composite materials up to 5 at% of MAC. This work has demonstrated the possibility of producing MAC-QC composite materials with acceptable and reliable properties.

A081

INFLUENCE OF MECHANICAL ACTIVATION ON SPHENE CERAMIC SYNTHESIS

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Sphene ($CaTiSiO_5$), a calcium titanosilicate ceramic has been prepared from a powder mixture of $CaCO_3$, TiO_2 and SiO_2 using vibro-miling for homogenization and activation precursors. The mechanochemical process initially yielded amorphous powders, which on further calcination, crystallized to yield sphene ceramic. The evolution of the phase composition with thermal treatment was investigated by X-ray powder diffraction (XRPD) and thermal analyses (DTA-TGA). Powder morphology and particle size distribution were analyzed by scanning electron microscopy (SEM) and laser diffraction, respectively. Optical dilatometry was used to measure the shrinkage behaviors of green bodies. The Rietveld refinement was employed to get the structural information of the synthesized powder. Densification and microstructure evolution was determined by means of density and scanning electron microscopy (SEM) measurement.

A082

AN INFLUENCE OF TEMPERATURE ON THE PROCESS OF CHEMICAL INTERACTION OF THE MEHANOSYNTHESIZED COPPER COMPOUNDS WITH LIQUID GALLIUM AND ON THE OBTAINED PRODUCT CHARACTERISTICS

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The aim of the work is to investigate the influence of temperature on the kinetics as well as structural and morphological characteristics of the products of chemical interaction of the mehanosynthesized copper compounds with liquid gallium. The temperature increase results in the change of the kinetics of interaction between a solid metal and a liquid one due to the acceleration of diffusion processes and due to the formation of additional phases.

The structural and morphological characteristics of the obtained products alloys are investigated by methods of the atomic force microcopy (AFM), scanning electronic microcopy (SEM) using back-scattered images and X-ray analysis. The work is carried out under the Integration Project of SB RAS No 138 and BRFFI No T09CO-014.

A083

THERMOMECHANICAL CHARACTERISTICS OF ARSENIC-SULPHIDE GLASS DOPED WITH BISMUTH

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Characterization of amorphous materials in terms of mechanical and thermomechanical properties significantly affects the range of their application. In that sense, in the process of thermomechanical examinations of glasses of the $Bi_x(As_2S_3)_{100-x}$ system, the temperatures of following processes have been detected: the begining of brittleness disappearance, glass transition temperature T_g, boundary between visco-plastic and liquid phase, the begining of the full glass liquidity. Moreover, using dilatometric analysis, we determined thermal coefficients of expansion of solid phase and visco-plastic phase. Microhardness of the examined glasses was determined by Vicker's method, with progressive load increase. Based on the model of elastic / plastic deformation EPD, the correction of experimental values was made. Morphology of the mechanically treated surfaces was investigated using scanning electron microscopy. The results of measurements were discussed and analyzed in the context of the influence of the composition complexity on the values of given parameters.

A084

CRYSTALLINE/MAGNETIC STRUCTURE OF $LA_{0.54}PR_{0.11}PB_{0.35-X}SR_XMNO_3$ OBTAINED BY HIGH-ENERGY MILLING

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Fine particles of $La_{0.5}Pr_{0.2}Pb_{0.3-x}Sr_xMnO_3$ manganites were prepared by mechanical alloying (MA), starting from the precursors, as La_2O_3, Pr_6O_{11}, $SrCO_3$, PbO and Mn_2O_3. In the initial stage takes place the formation of nanocomposites at the contact surfaces between different crystallites. After the ball milling (10-100 h) small particles, highly deformed were obtained. The thermal treatment was performed on the pressed samples between 900 and 1300 K, in air during 10 h. The phase composition, microstrains, coherent block size and lattice constants were obtained from XRD data, while the Curie temperature and metallic phase concentration were obtained from variation of specific/molar magnetization vs temperature. A dependence of the Curie and the transition temperatures from metallic to insulator state with the milling duration was observed.

A085

INFLUENCE OF HIGH-ENERGY MILLING ON THE STRUCTURE AND TRANSPORT PROPERTIES OF $LA_{0.54}HO_{0.11}CA_{0.35}MN_{1-X}CR_XO_3$

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The samples with the chemical composition $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-x}Cr_xO_{3-\delta}$ were prepared by means of sol-gel method and finally treated at 1200°C for 5 hours in air. The samples were milled for 10 hours in a high energy mill, pressed into pallets and treated for 10 hours at 850 °C. The samples were studied by XRD; data were handled by means of the FULLPROF code. We measured the specific magnetization by using a Foner type magnetometer, between 77 and 350 K, at 1.7 T magnetic field intensity. The resistance was measured between 7 and 330 K, by using a closed cycle refrigerator, and H_{max} = 0.9 T. Two series of samples were investigated: first, treated at 1200 °C and the second, obtained by milling and treated at 850 °C. We discussed the results concerning the change of the structure, magnetic and transport properties in function of the Cr concentration.

A086

NON-THERMAL EFFECTS UNDER MICROWAVE HEATING OF SOLIDS AND MATERIALS

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The microwave-heating rate has a strong functional relationship to the dielectric properties (particularly dipole mobility) and electric field strength. So, the efficiency of microwave radiation absorption should be minimal for solid organic and inorganic compounds. We have investigated features of microwave absorption for some intercalative compounds of fluorinated carbon with organic reagents. The experiments have been carried out in microwave system "Explorer-48", equipped with video camera. This accessory allows to record video of reagent changes under microwave irradiation. The specific feature of heating the intercalated compounds of fluorinated graphite is transparency of fluorographite matrix for the microwave radiation passage, thus heating of the reaction mass occurs due to absorption of microwave energy by intercalated (embedded in a matrix fluorographite) compound. It has been found that the effectiveness of microwave heating for fluorinated graphite intercalation compounds depends on the dielectric properties of the organic reagent embedded. After the decomposition of these compounds and the formation of nanostructured carbon, the appearance of high-frequency corona discharge on carbon fibers has been recorded by video camera. The formation of high frequency discharge explains features of temperature and pressure fluctuations in the experimental vial under microwave heating of intercalative compounds. On the other hand, this phenomenon indicates on high-density microwave energy in the cylindrical resonator of our microwave system.

The formation of high-frequency corona discharge on the surface of materials is characteristic feature for microwave heating of solid compounds with small-sized structures (cracks, dislocations, fibers and small-sized crystals). These effects were obtained under microwave syntheses of volatile coordination compounds of precious metals. Local surface discharges are characterized by high electron density and high local temperatures. This leads to the decomposition processes of the initial and intermediate compounds. In addition, the local high-temperature reaction can occur at relatively low average temperatures of the material. So, short-time exposures of microwave discharges led to oxidation of nanostructured carbon material. These effects may be useful for surface modification of materials and substances. However, high frequency discharges can lead to degradation of the reaction products and significantly reduce of the target products yield in the case of synthesis under solvent-free conditions.

This work was supported by grant № 11.G34.31.0033 Government of the Russian Federation for State Support of scientific research under the guidance of leading scientists in the Russian educational institutions of higher education on 24 November 2010.

A087

THE SMART PROCEDURE OF NATURAL PRODUCTS ISOLATION

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Natural products are the base of many medicinal remedies. Routine technology of their isolation is extraction. This technology requires high consumption of toxic organic solvents, produces detrimental waste, and therefore is environmentally unsafe. The aim of our research was to develop an effective and ecologically friendly method of natural products isolation from plant material. We have applied the smart method of mechanochemical isolation based on combined high-energetic mechanical treatment of plant material with certain adsorbents. In such a technology we have used planetary and vibration accelerated grinders. It has been sown the influence of sorbents addition (their nature and quantity) on the yield of alkaloids from Aconitum roots, Sophora roots and Saxaul sticks. The dependence of yield on polar properties of solvent used for treatment a reaction mass has been studied as well. The natural products have been obtained with higher yield as compared with usual extraction and in some cases with higher selectivity.

This work was supported by grant № 11.G34.31.0033 Government of the Russian Federation for State Support of scientific research under the guidance of leading scientists in the Russian educational institutions of higher education on 24 November 2010.

A089

MECHANOCHEMISTRY AND THE OTHER BRANCHES OF CHEMISTRY: SIMILARITIES AND DIFFERENCES

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The classification usually attributed to Ostwald distinguishes the branches of chemistry according to the form of energy inducing the reactions. In thermochemistry, processes are activated by thermal motion; the available energy is of the order of kT, about 25 meV at room temperature. A visible photon carries a few eV of energy, making reactions with much higher activation energy possible. The situation is analogous in the case of mechanochemistry. Mechanical action (ball milling, high pressure - torsion) results in plastic deformation, that concentrates the external work into slip planes and there into dislocations. It is argued, that this concentration of energy makes unique reactions possible. As some mechanical energy is converted to heat, mechanochemical reactions are always mixed with thermally activated processes.

A090

MECHANOCHEMICAL SYNTHESIS OF MgH_2-TiB_2 COMPOSITES FOR HYDROGEN STORAGE

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Hydrogen storage is a key enabling technology for the development of hydrogen and fuel cell power technologies in transportation, stationary and portable applications. On-board hydrogen storage is considered to be the most challenging aspect for the successful transition to a hydrogen economy. Modified nanostructure materials offer promise for superior hydrogen storage due to short diffusion distances, new phases with better capacity, reduced heats of adsorption/desorption, faster kinetics. High energy mechanical milling was used to synthesize MgH_2 (90 wt.%) + TiB_2 (10 wt.%) composite as possible solution for hydrogen storage. XRD and SEM analysis was used to determine microstructure and morphology while the DSC analysis was used to resolve the hydrogen desorption properties. It has been shown that use of nanostructurated TiB_2 decrease the MgH_2 desorption temperature.

A091

FLUORINE INCORPORATION FROM PTFE TO TITANIA NANOPARTICLES BY COMBINING MECHANICAL STRESSING AND ANNEALING

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Incorporation of fluorine from poly(tetrafluoro ethylene) (PTFE) into titania nanoparticles at their boundaries via combined mechanochemical and annealing routes were examined. Increasing the milling time increased the amount of fluorine incorporated into titania, $F_{Titania}$, evaluated by XPS and EDXS. Changes in the ^{19}F-MAS-NMR spectra include broadening of the -CF_2- based peaks in PTFE and appearance of several new peaks. The latter are associated with the partial decomposition of PTFE and the change in the states of fluorine species from those in PTFE and its fragments to $F_{Titania}$. Conversion of fluorine species to $F_{Titania}$ is a consequence of the introduction and partial substitution of oxygen vacancies, Vo, in the $TiO_{6-x}Vo_x$ deformed octahedral units, with fluorine from the partially decomposed PTFE. These mechanochemical processes are promoted by the formation of near surface non-crystalline states of titania and partial reduction of Ti^{4+} to Ti^{3+} by the nearby Vo, as inferred from HRTEM and UV-Vis-NIR spectra, respectively. Upon annealing the co-milled samples in air, the concentration of $F_{Titania}$ decreased. Simultaneously, the ^{19}F-NMR spectra exhibited unique change. Apart from the disappearance of the PTFE-derived organic species, appearance and growth of new broad peaks were observed. These suggest the disproportionation of the F_{Titani} species upon annealing, i.e. partly by reoxidation and partly by penetration into solid interior to form oxyfluoride like states.

A092

SURFACE HARDENED Al ALLOYS PREPARED BY HIGH-ENERGY BALL-MILLING USING VARIOUS PROCESS CONTROL AGENTS

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Al alloys is one of promising candidate materials to replaces steels in various structural machinery parts where light weight is required. However, they lack appropriate heat treatments for surface hardening which can be easily accomplished by a variety of ways in steels. In this work, we present a new processing route to surface-harden Al alloys employing mechanical milling. Pure or pre-alloyed Al powders were ball-milled in an ammonium atmosphere using some specific process control agents (PCA). The PCAs were inexpensive and nontoxic organic compounds containing N, C, O and H. During the milling, Al-N-C-O based-amorphous phases formed without formation of crystalline nitrides, oxides or carbides. The metastable phases gradually transformed upon heat-up to nanocrystalline Al-N-O and Al-C-O which are embedded in Al matrix. Conventional sintering of the ball-milled powders resulted in the formation of isotropic Al-based particulate nanocomposites. By proper control of sintering atmosphere, however, we could obtain Al alloys where the hardness and the wear resistance of surface are markedly increased.

A093

EFFECT OF THIRD ELEMENTS ON THE PARTICLE SIZE OF DISPERSOIDS IN MECHANICALLY ALLOYED Ni-Cr-Y_2O_3 ALLOYS

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Ni-based superalloys have recently attracted much attention for possible application ions at high temperatures in powder plants. They are, in particular, important for various core parts in advanced reactors such as the GEN IV reactors, due to their excellent oxidation and corrosion resistance at high temperatures. However, conventional strengthening by precipitation is insufficient for these alloys due to coarsening of precipitated particles. Mechanical alloying offers an ideal way to overcome this problem by introducing oxide as reinforcing particles. In the present work, we synthesized Y_2O_3-reinforced Ni-Cr-alloys by mechanical milling. In spite of generally known inertness of oxide with metals, Y_2O_3 was completely dissolved within the Ni-Cr matrix during mechanical milling at ambient temperature, forming Ni-based solid solution. Y-O or Cr-Y-O particles gradually precipitated from the solid solution by subsequent annealing at high temperatures. The addition of a third element to Ni-Cr-Y_2O_3 played an important role in controlling the sized of dispersing and precipitated particles, and thus influencing the mechanical properties.

A094

STRUCTURAL AND ELECTRICAL PROPERTIES OF Yb SUBSTITUTED Zn-FERRITE OBTAINED BY HEBM

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Mechanochemical synthesis of $ZnFe_{1.95}Yb_{0.05}O_4$ was performed in a planetary ball mill "pulverisette 4" equipped with tungsten carbide bowls and balls. Balls of 10 mm in diameter and a 250 ml bowls were used, ball-to-powder mass ratio was 20:1. X-ray powder diffraction (XRPD) data (*in situ* and *ex-situ* measurements) were collected on a PANalytical X'pert PRO MPD diffractometer. *In situ* measurements were made at room temperature and in the temperature interval 100-600 ºC, in steps of 100 ºC. After annealing at temperatures 300 ºC, 400 ºC, 500 ºC, 600 ºC, 700 ºC, 800 ºC, diffraction pattern were collected at room temperature (*ex-situ* regime). The collected XRPD data of as-prepared sample confirmed successful mechanochemical synthesis of spinel, as well as the presence of hematite and tungsten carbide. The X-ray data were used for the refinement of the structure parameters (lattice parameters and cations occupancies) and for microstructure (crystallite size and microstrain) determination. The increase of unit cell with the increase of thermal annealing temperature was evident in both *in situ* and *ex-situ* regimes with different parameters of linear tendency. It was found that crystallite size increased, in both regimes, from ≈7 nm to ≈11 nm with the increase of annealing temperature up to 600 ºC. HRTEM measurement gave results consistent with XRPD, particle size increased with the increase of temperature. Refinement of occupational parameters confirmed high disordering at octahedral and tetrahedral sites in the structure of as-prepared $ZnFe_{1.95}Yb_{0.05}O_4$. The found cation distribution for both regimes showed ordering tendency with the increase of temperature. Occupation parameters of Fe^{3+} at octahedral sites for *ex-situ* measurements were slightly lower than corresponding *in situ* values. Impedance analyzer HP-4194A was used to measure the material properties in the frequency range from 100 Hz to 40 MHz at room temperature. As-prepared sample as well as samples annealed at 500 and 800 ºC were measured. Resistivity decreased with increasing frequency for all samples. As-prepared sample had the lowest resistivity while the highest resistivity was for sample annealed at 500 ºC, within all measured frequency range. The real part of the dielectric constant decreases continuously with increasing frequency only for as-prepared sample. The low value of dielectric loss indicates that the samples are suitable for high-frequency applications.

A095

CHANGING OF CHELATION ABILITY OF HUMIC ACIDS UNDER MECHANICAL ACTIVATION

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Mechanochemical activation of humines allows modification different properties of this substance purposefully. Mechanochemical activation of peat and oxidation of humines by oxygen and peroxides leads to varying of soluble product molar mass. The oxygen active groups as –OH and –COOH content changing was found too. These groups are responsible for heavy metal chelation and dissolution of silica. A modification may be explained by selective bond breaking of phenol biopolymer under mechanical activation. Computer simulation of humic acid degradation under different conditions was made with aim to determine decomposition leading directions. The model operated with active oxygen groups content changing during transformation. Computer simulation of thermal and mechanochemical ways of transformation described the changing of chelation ability of humic products.

A096

THE HIGH TEMPERATURE FINE GRINDING OF POLYMERS UNDER ACTION OF INTENSE SHEAR STRESS AS A MECHANOCHEMICAL AVALANCHE-LIKE CRACKING PROCESS OF POLYMERS

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A new conception to explain the non-trivial kinetics peculiarities of the high temperature fine grinding of polymers in the air under action of intense shear stress has been developed. According this conception the grinding of shear stressed polymers can be realized in the form of a branched chain mechanochemical process – in the form of avalanche-like cracking. The entire set of non-trivial kinetics peculiarities of the high temperature fine grinding of semicrystalline polymers in the air under action of intense shear stress were explained. There were found three effects: 1. Possibility of the energy saving technology using for semicrystalline polymers shear grinding at enhanced temperatures (near the melting temperature T_m of the investigated polymer); 2. Extreme temperature dependence of the fracture rate of stressed semicrystalline polymers; 3. "High temperature embrittlement" of Low-Density Polyethylene.

A097

EFFECTS OF MECHANICAL ACTIVATION ON THE INTERACTION OF OLIVINE AND VERMICULITE WITH CARBON DIOXIDE

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Mineral CO_2 sequestration, known as “mineral carbonation” is concept where CO_2 is chemically combined in an exothermic reaction with silicate minerals to form carbonates and other stable by-products. The principle of this idea is to mimic natural weathering processes, under ambient conditions very slow - thousand to millions years.

Activation processes based on high-energy milling (mechanical activation) are used to modify the properties of materials, enhance the reactivity of minerals and produce advanced materials as a result of changing their solid-state properties. Mechanochemical carbonization is the one-step process in which mechanical activation is combined with carbon dioxide sequestration, resulting enhanced kinetics and economical feasibility of the carbonation process. The aim of the present paper is to investigate comparatively the physico-chemical properties of olivine and natural/heated/thermally exfoliated vermiculite mechanically activated in a planetary mill in the absence and presence of carbon dioxide gas. To identify the mechanically-induced changes in both silicate minerals X-ray diffraction/FT-IR analyses and specific surface area measurements were applied.

A098

MECHANOCHEMICAL PREPARATION AND SOLID-STATE CHARACTERIZATION OF COMPOSITES OF BETULIN AND ITS ETHERS

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Biological activity of betulin and its derivatives as antiviral, anti-inflammatory, antitumour agents is under intense investigation at present. One of the methods to increase the biological availability is to obtain compositions with carriers, in particular, with the help of mechanochemical methods. The mechanocomposites of betulin and its diacetate and dipropionate with the carriers were obtained by ball-milling. The methods of thermal analysis, X-ray diffraction, IR spectroscopy and HPLC-analysis were used to study the effect of mechanical activation on the individual compounds and their mixtures. The stability of betulin and its ethers under mechanical treatment was demonstrated. The formation of complexes and solid solutions in the ball-milled mixtures was shown by IR spectroscopy and thermal analysis methods. The work was supported by the grants of CRDF, RF Ministry of Education and Sciences and the RAS Program “Fundamental Sciences for Medicine”.

A099

Fe-Y_2O_3 NANOCOMPOSITE PREPARED BY BALL-MILLING: FORMATION MECHANISMS AND NANOSCALE CHARACTERISATION

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Reactive high energy ball-milling has known a growing interest from both fundamental and applied point of view. We focus here on the specific system Fe-Y_2O_3 metal-oxide nanocomposite because of its potential application to the synthesis of oxide dispersion strengthened steels, which are promising materials for nuclear applications. YFe_3 and Fe_2O_3 were ball-milled during different milling durations in the stoechiometric proportions defined by the chemical reaction $2\ YFe_3 + Fe_2O_3 \rightarrow 8\ Fe + Y_2O_3$. The obtained milled powders were characterized by XRD, SEM, TEM and their thermal behaviour was investigated by DTA. Through those characterizations, a mechanically induced Self-propagating Reaction (MSR) was observed. The material has been also analysed by Atom Probe Tomography (APT) after ball-milling and annealing. The as-milled material is constituted by two nanometric interconnected phases: α-iron super-saturated in Y and O and an amorphous yttrium and oxygen rich phase, with a ratio O/Y close to 1. After annealing, the system tends toward equilibrium state: a pure α-iron phase and cubic Y_2O_3 oxide. However, a small amount of Y and O remains in the iron phase, and yttrium oxide is slightly sub-stoechiometric in oxygen.

A100

MECHANOCHEMICAL PREPARATION OF ORGANIC-INORGANIC HYBRID MATERIALS OF DRUGS

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The composites of piroxicam and meloxicam with alumina, boehmite and gibbsite were prepared by ball-milling using AGO-2 (ISSC, Russia) and Pulverisette 6 (Fritsch, Germany) planetary mills. The X-ray diffraction peaks of drugs disappeared in the milled samples indicating the amorphization of the drugs during milling. The changes in the IR spectra suggested the interaction of the components during ball-milling. XPS analysis confirmed the interaction of the functional groups of the drugs with the surface of the carriers. The dissolution behaviour of drugs from the ball-milled mixtures revealed that the drugs release can be altered by changing the substrate. The rate of drugs dissolution was higher, probably because of the formation of core-shell mechanocomposites characterized by increased surface of the drugs present in amorphous state. The work was supported by RFBR (09-03-92658) and Indian Ministry of Science and Technology.

A101

FOLLOWING THE PRODUCTS OF MECHANOCHEMICAL SYNTHESIS STEP AFTER STEP

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A detailed study of mechanochemical processes using specially designed model devices for controlled mechanical treatment may give a much better insight into the mechanisms of mechanochemical reactions. We describe several experiments on co-grinding molecular solids in a special device, which permits to quantify the energy input into a solid sample and to follow the products of mechanochemical synthesis step by step. The application of the device is tested on the systems, in which two products can be formed concomitantly or in a sequence on co-grinding. The work was supported by grants from RFBR (08-03-00143, 08-03-012130, 09-03-00451, 09-03-92658, 10-03-00252), a BRHE grant from the CRDF (RUX0-008-NO-06), projects 21.44 and 5.6.4 of the Russian Academy of Sciences, and the FASI (RF) Contracts №02.740.11.5102 and GK P2529.

A102

SELECTIVE EFFECT OF CARBOXYLIC ACIDS ON POLYMORPHISM OF GLYCINE AND CO-CRYSTAL FORMATION

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The results of co-grinding of dry mixtures of glycine with carboxylic acids are compared with the outcome of crystallization experiments. Small amounts of carboxylic acids added to aqueous solutions or to dry samples of α-glycine subjected to mechanical treatment were shown to favor crystallization of γ-glycine. Stoichiometric amounts of additives of carboxylic acids to solutions or mechanically treated solid mixtures with α-glycine give glycine co-crystals for some acids, and no products for the other. A co-crystal of glycine with glutaric acid is the first example of a glycine co-crystal which is not a salt. This work was supported by grants from BRHE (RUX0-008-NO-06), RFBR (08-03-00143, 10-03-00252 and 11-03-00684), by the Integration Projects 13 and 109 of the Siberian Branch of RAS, Projects 21.44 and 5.6.4 of RAS, and a FASI Contract П2529. The authors thank A. F. Achkasov for technical assistance.

A103

'HEDVALL EFFECT' IN CRYOGRINDING OF MOLECULAR CRYSTALS. A CASE STUDY OF A POLYMORPHIC TRANSITION IN CHLORPROPAMIDE

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The effect of grinding at ambient temperature and at 77 K (CryoMill Retzsch) on the polymorphic transitions in α- and ε- chlorpropamide has been compared. The result of grinding of α-chlorpropamide at room temperature could not be interpreted as a mere formation of traces of ε-polymorph. The diffraction patterns suggested the presence of small amounts of some unknown polymorph, possibly in a mixture with other polymorph(s). Possibly, mechanical treatment gave a defect nanostructured phase with alternating domains. Cryogrinding of α-chlorpropamide did not result in polymorphic transitions. In contrast to that, cryogrinding of ε-polymorph was much more efficient, than grinding at ambient temperature: almost no changes could be observed at ambient temperature, whereas cryogrinding gave α-form. The observed phenomena could be interpreted taking into account that at low temperatures ε-polymorph undergoes a polymorphic transition into another polymorph - ε'-form. Without grinding, ε'-form transforms back to ε-polymorph when heated back to ambient temperature. If grinding takes place in the temperature range of the ε- to ε'- polymorphic transition, the transformation to α-form occurs. One phase transition, induced by low temperature, facilitates another one, induced by mechanical treatment. The reason for this interesting phenomenon is to be sought in the similarity of crystal packing of molecules with different molecular conformations in ε- and ε'-forms, and of the similarity of molecular conformations despite different crystal packing in ε'- and α-forms. This work was supported by grants from BRHE (RUX0-008-NO-06), RFBR (08-03-00143), by the Integration Project 109 of the Siberian Branch of RAS and a FASI Contract 16.740.11.0166. The authors thank Mr. A. Achkasov for technical assistance.

A104

DECREASING PARTICLE SIZE HELPS TO PRESERVE METASTABLE POLYMORPHS. A CASE STUDY OF DL-CYSTEINE

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Mechanical grinding is widely used to obtain "active forms" of organic crystals. There is another aspect of possible effects of grinding on the properties of molecular solids, which has up to now received less attention. Some phase transitions were reported to be complete if propagating in single crystals, but not in powder samples. This property of small particles may be important for practical applications, for example, for increasing the shelf-life of active metastable pharmaceutical forms and their kinetic stability with respect to variations in temperature and pressure. Interestingly enough, "resistance to phase transitions" of molecular crystals was observed for the particles in the μm size range, whereas for inorganic systems a similar phenomenon is known for nanoparticles. The contribution describes the effect of particle size on the interconversion between the high-temperature (I) and the low-temperature (II) polymorphs of crystalline DL-cysteine ($^{+}NH_3$-CH(CH_2SH)-COO^{-}) studied by X-ray powder diffraction, Raman spectroscopy, differential scanning calorimetry, scanning electron microscopy. The effects are interpreted in terms of kinetic control of the polymorphic transitions and the relation between particle size, nucleation of a new phase, relaxation of mechanical stresses. This work was supported by grants from BRHE (RUX0-008-NO-06), RFBR (08-03-00143), by the Integration Projects 13 and 109 of the Siberian Branch of RAS, Projects 21.44 and 5.6.4 of RAS, and a FASI Contract 16.740.11.0166. The authors thank Dr. A.A. Ogienko, Dr. N.A. Rudina, Dr. L.S. Aladko, Dr. A.S. Yunoshev, S.A. Myz, A.F. Achkasov for technical assistance.

A105

MONITORING MECHANICAL PROPERTIES OF INDIVIDUAL HYDROGEN BONDS: SINGLE-CRYSTAL X-RAY DIFFRACTION AND POLARIZED RAMAN SPECTROSCOPY IN SITU

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The studies of molecular crystals at non-ambient conditions help to understand intermolecular interactions and their role in the formation of crystal structures and in their response to external actions. Crystals of amino acids are of special interest in this respect because the structure-forming units in these crystals are similar to those in the biopolymers and can be used as biomimetics. Single-crystal X-Ray diffractions and polarized Raman spectroscopy make it possible to follow the changes in the individual hydrogen bonds with pressure in details. The two techniques give complementary information: diffraction experiments provide data on the changes in atomic coordinates averaged over space and time; a detailed spectroscopy study can help in understanding the dynamic processes related to pressure changes (compression of individual intermolecular hydrogen bonds, rotation of molecules as a whole and of the individual molecular fragments). In this work structural changes in DL-serine and L-serine were compared in the pressure range 0.2 – 4.3 GPa using an Almax-Boehler diamond anvil cell to create hydrostatic pressure. The lengths of intermolecular hydrogen bonds linking amino-groups and serine side chains in the crystal structure were followed *vs*. pressure. The rotation of carboxylic groups of serine with increasing pressure was followed. This work was supported by grants from BRHE (RUX0-008-NO-06), RFBR (09-03-00451), by the Integration Projects 13 and 109 of the Siberian Branch of RAS, Projects 21.44 and 5.6.4 of RAS.

A106

SHS OF SYSTEM WITH ACTIVATED SILUMIN

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The study has included synthesis of the activated silumin powders and accomplishment of the complex X-ray phase analysis. The X-ray analysis has revealed that the basic phase is the aluminum solid solution with lesser amount of the solid silicon solution. Broadening of the X-ray reflexes basically occurs for two reasons: micro-diffraction and reduction of the coherent dispersion areas. Metallic manganese has been obtained by the metallothermal method in SHS-regime. It is shown that the use of silumene as a reducing agent results in a high degree of manganese extraction from manganese monoxide as both components of silumene – aluminum and silicon take part in SH-synthesis with a reduction stage. Preliminary activation of the reducing agent is to carry out the process at the temperature of the furnace 750 – 800 ^{O}C.

A107

PROPOSAL OF A NEW MECHANOCHEMICAL PHASE DIAGRAM FOR THE BINARY SYSTEM Cu-Zn

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A set of Cu-Zn alloys with Zn percentages ranging from 30% to 90% have been synthesized by mechanical alloying. The study of the intermediate phases as a function of the grinding time has shown that the reaction is started with the initial formation of phases very rich in zinc like the ε phase that continues reacting with copper until reaching the expected composition from the stoichiometric ratio copper/zinc of the starting mixture. This behavior suggests that the mechanical alloying takes place trough a mechanism that implies the diffusion of copper into the zinc matrix. On the other hand, it has been demonstrated that the grinding extends considerably the Zn composition range at which α and β phases becomes stabilized with regards to the conventional Cu-Zn phase diagram. A mechanochemical Cu-Zn binary phase diagram at room temperature has been proposed.

A108

SOLVENT-DROP GRINDING SYNTHESIS OF MELOXICAM CO-CRYSTALS

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Obtaining co-crystals of drugs is becoming a widely used method of improving the bioavailability of Active Pharmaceutical Ingredients (API). Co-crystals of API with co-crystal formers are multi-component crystals, in which components alternate orderly. Different methods are used, to obtain pharmaceutical co-crystals, such as co-crystallization, co-melting, spray-drying, etc. However, it is the mechanochemical method, in particular, solvent-drop co-grinding, which is considered as the most promising one. In the present work we illustrate the possibility to generate over dozen of meloxicam co-crystals with various carboxylic acids by solvent-drop co-grinding. We discuss in more details the crystal structures of meloxicam-succinic acid, meloxicam-adipic acid and meloxicam-therephthalic acid co-crystals in relation to their properties, including the dissolution profile in a comparison with the crystals of individual meloxicam.

A110

OPTICAL PROPERTIES OF NICKEL MANGANITE CERAMICS OBTAINED FROM MECHANICALLY ACTIVATED POWDERS

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Stoichiometric mixture of manganese and nickel oxide powder calcined at 1050°C was additionally mechanically activated in a high energy planetary ball mill for 5-60 minutes to obtain a pure $NiMn_2O_4$ phase. The powders were pressed and sintered for 60 minutes at 900°C, 1050°C and 1200°C. Morphological changes of nickel manganite ceramics were monitored using scanning electron microscopy, while structural characteristics were followed using X-ray diffraction. Far infrared reflectivity spectra at room temperature for all sintered samples were recorded in the frequency range between 50 and 1200 cm^{-1}. Transversal and longitudinal optical modes were calculated for six ionic oscillators belonging to the partially inverse spinel structure of nickel manganite.

A112

CHARACTERIZATION OF COMPLEX OXIDES PREPARED BY BALL MILLING

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The properties of nanomaterials are sensitive to microstructural and structural parameters, which in turn strongly depend on the preparation method. There is a challenge to improve physical performance (magnetization, coercivity, conductivity, photoluminescence, etc.) by varying microstructural parameters (such as particle size and shape, strain and their anisotropy) using new or modified synthesis procedures. Among the many types of preparation techniques, the nonconventional mechanochemical synthesis has been recognized as a powerful route to novel, high-performance and low-cost nanomaterials.

This work is focused on the characterization of nanocrystalline oxides prepared by high energy ball milling. Structural and microstructural parameters of as-prepared samples have been investigated by various methods such as X-ray diffraction, X-ray photoelectron spectroscopy, nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy and transmission electron microscopy. To analyse the microstructural parameters (crystalline size and strain), the full-profile analysis, Warren-Averbach and simplified integral breadth method were used. The correlation between particular methods used for local structure investigation of nanocrystalline oxides has been discussed.

The present work was supported by the „Japan Society for the Promotion of Science“. Partial support by the Slovak Research and Development Agency (Grant APVV-0189-10 and SK-SRB 0019-09), the Scientific Agency of the Ministry of Education of the Slovak Republic and of the Slovak Academy of Sciences (Grant VEGA 2/0139/10) and DAAD is gratefully acknowledged.

A113

DEVELOPPING OF MAGNESIUM AND MAGNESIUM-SCANDIUM SYSTEMS WITH OPTIMIZED HYDROGEN SORPTION FOR VLi BATTERIES APPLICATION

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It was established in last decades that MgH2 has attractive properties as H storage material due to its high reversible storage capacity (i.e. 7.6 wt.%), light weight and low cost. It can also be successfully applied in electrochemical systems such as accumulator batteries, namely Li-ion batteries as anode material. Process of insertion of Li in graphite, that take place in nowadays Li batteries is replaced by conversation chemical process according to:

$$MgH2 + 2\ Li^+ + 2\ e^- = Mg + 2\ LiH$$

The advantage of this cell consists in the combination of the high gravimetric and volumic capacities of MgH2 with the high energy density of lithium ion batteries and for this reasons it presents promising opportunity. Both ways of hydrogen releasing, stored in MgH2 (via gas phase or electrochemically), demand the achievement of good sorption-desorption kinetic. Magnesium exhibits very slow sorption kinetics and to solve this problem, different paths were proposed. Thus, it was shown that fluorite-type structure of material is one of the key factors to favor hydrogenation kinetics, because of the formation of both tetrahedral and octahedral sites, occupied by H, and is preferable than rutile-type of pure MgH2. It was shown that Mg and Sc alloys which have fluorite-type structure have very high reversible storage capacity (5.6 wt.%). Addition of Ni and Pd allows improvement of the kinetics of hydrogen sorption of Mg. We propose to deposit on the surface of Mg-Sc alloys (65-80at.%Mg) palladium nanoparticles by means of decomposition of palladium hexafluoroacetilacetonate in super critical fluid conditions (SCF), as it was performed in previous works. This method, developed in the last years, open a variety of possibilities allowing to perform impregnation of support surface by well-distributed and small size particles. It was established that sorption kinetic is controlled by two phenomenons: nucleation and diffusion of hydrogen through MgH2 layer. Velocity of the last one is extremely low, so to provide entire hydrogenation, it is necessary to increase specific surface area via reducing particles size. The most widespread method to provide that is ball milling of magnesium under hydrogen atmosphere that permit to achieve good characteristics. On the other side, material obtained by this way with high-surface area oxidizes much more easily, particularly during charge-discharge cycles that result in degradation of H capacity. Therefore, we suggested protecting nanoparticles of MgH2, synthesized in SCF conditions, from oxidation as well as coarsening by covering them with thin copper layer. As precursor for copper deposition copper ethylate will be used.

A114

MULTIFERROIC PEROWSKITE MATERIALS OBTAINED BY REACTIVE GRINDING

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$BiFeO_3$ is the most studied multiferroic materials because it presents multiferroic properties at room temperature. Many sophisticated methods have been proposed for the synthesis of this compound, but in most of cases small amount of impurity phases, that damages the physical properties of this material are present. A pure phase of BiFeO3 has been prepared by us by mechanochemical synthesis from stoichiometric amounts of Bi_2O_3 and Fe_2O_3. Experimental conditions to prepare this material are presented. It has been shown that the control of the partial pressure of oxygen during grinding is crucial for achieving a pure $BiFeO_3$ phase. The resulting samples are characterized in terms of their structure and microstructure using different experimental techniques such as X-ray powder diffraction, electron microscopy, specific surface area measurements, DSC, TMA.

A115

ELEMENTARY ENERGETIC AND KINETIC CONSIDERATIONS IN THE MECHANOCHEMICAL SYNTHESIS OF FE-C ALLOYS AND COMPOUNDS

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Some elementary considerations including chemistry and continuum mechanics concepts are considered, using experimental data produced by the authors in the past by means of mechanochemical processing of powders of Fe and C at initial stoichiometric composition of 6.67 % atomic carbon. While the focus of previous work was on the synthesis of metastable iron carbides the attention here is devoted to the phase evolution in the first stages of milling. Results obtained with a SPEX 8000 mill in a time span ranging from 900 to 18000 s are discussed in the framework of an elementary kinetic model previously developed and with the aid of some very simple concepts of continuum mechanics.

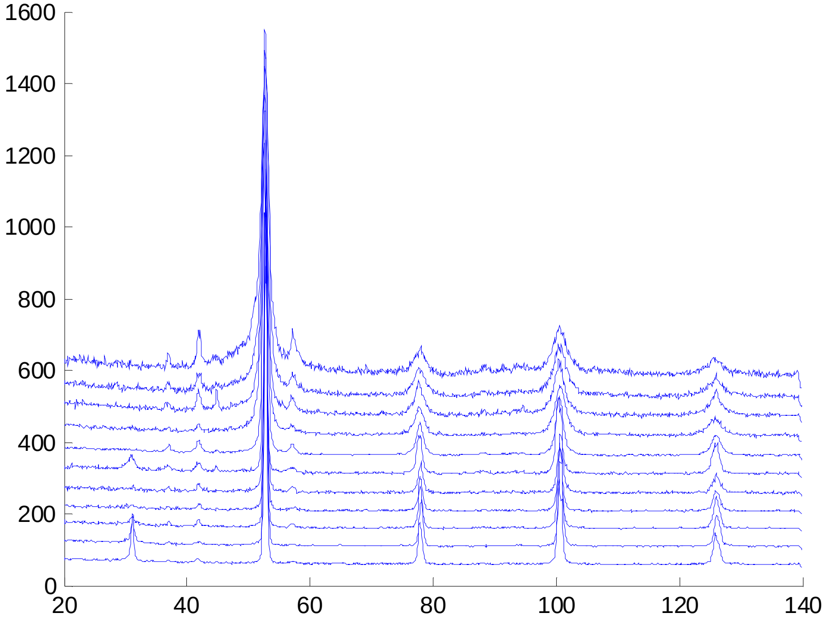

Fig. 1 XRD evolution of mechanically alloyed powders Fe C powders, with processing times from 900 s up to 18000 s

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A116

MECHANOCHEMICAL TRANSFORMATIONS IN Ti/B/H_2 SYSTEM

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Morphological, structural and chemical evolution in Ti/B/H_2 system was studied in detail as a function of mechanical treatment. Ti/B powder continuously changes both in composition and morphology during ball-milling in H_2 flow, as follows: (1) initial mechanical activation induces Ti – H_2 reactivity; (2) the powder composition varies from Ti/B to TiH_{2-x}/B causing a change in mechanical properties. The role of boron additive also changes from preventing the Ti particles from sticking together in the early stages to a matrix material participating in Ti – B interface reactions in the intermediate and final stages of the process. Boron atoms participating in the formation of nanoscopic holes give rise to new H states in the hydride by changing the local atomic state of Ti atoms. The dynamics of morphological transformations in Ti-B-H_2 system and their interrelation with Ti – H_2 reactivity were studied using different structural, microscopic and spectroscopic techniques.

This work was done with partial support of RFBR (Projects No. 10-03-00942-a and No. 08-02-00148).

A117

TO THE PROBLEM OF GENERATION OF NON-EQUILIBRIUM POINT DEFECTS AND ANOMALOUS DIFFUSION IN NANOSTRUCTURES OF METALS DURING MECHANICAL ALLOYING

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Processes of structural changes which account for the generation of non-equilibrium point defects and anomalously fast diffusion of interstitial impurities in nanostructured metals and alloy during plastic deformation are studied. Extra vacancies generated by intercrystalline boundaries in their migration are shown to be the main cause of the diffusional mass transport enhancement. Non-equilibrium vacancy concentration profiles are calculated for nanostructures with grain size 5-100 nm under mechanical alloying conditions. It is shown that in materials with grain size larger than 100nm the diffusion enhancement occurs only in the regions near the grain boundaries, whereas at grain sizes smaller than 10 nm the enhancement is possible even in the grains bulk. The effect of interstitial atoms on the diffusion and processes of recrystallization is negligible.

A118

THE USING OF SYNCHROTRON RADIATION FOR MECHANOCHEMICAL PROCESS INVESTIGATION: MODEL AND REAL EXPERIMENTS

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The enormous collected experimental data on mechanochemical processes contains no information on the initial phase of reaction, i.e., transmission of external energy from the active elements of the activator to the crystal lattice and adaptation of this energy by the crystal. Thus, there are no data on the crystal lattice behavior under fast dynamical loading and at unloading. To correctly interpret the obtained mechanochemical data it is necessary to know the conditions they are realized in.

This work implements a nanosecond resolution X-ray diffraction experiment on synchrotron radiation (SR) beams, when crystal lattice behavior under dynamical (shock) loading was studied in real time, i.e., in situ, on model systems. In an experiment modeling an elementary act of mechanochemical impact, a sample was subjected to a shock impact of the striker (usually we apply aluminum, copper or nickel plates), shot from a gas-dynamic gun. The striker accelerated under the impact of products of explosion of high explosives in the gun. An aluminum striker can accelerate up to a velocity of 3 km/s (a minimum velocity is 0.5 km/s). Upon knocking a sample, also plate-shaped, the striker produces a shock wave in the sample. X-ray photography (32 frames) is performed ~ 100 ns after the shock wave generation. A series of X-ray pictures was recorded with a time resolution of 125 ns and an exposure of 1 ns. Diffraction data obtained in this experiment allows getting information on the loading of a sample under study with a shock wave, i.e., on the energy transmission to a crystal lattice from equation of state.

Relaxation processes is very important question in mechanochemistry but not enough information about available at the moment. Information on unloading processes was received in SR experiment immediately after the shock impact is of high importance. These data are also obtained from a diffraction experiment with high time resolution. We have found that “fresh” product (5-80 ns after their formation) are not resistant to a shock action (an impact on an obstacle with a velocity of 2 km/s); their crystal lattice was destroyed. Precisely the same particle but after 250 ns nucleation can withstand an impact. We have also found that this relaxation processes in product has strong temperature dependence. This result is very important for design of new more effective mechanochemistry activators.

The relaxation processes in different metals (Ag, Ni, Cu) with millisecond time resolution was investigated at different temperature. The activation energy was found in air and solution environment for these metals.

A119

CHARACTERIZATION OF MECHANOSYNTHESIZED NON-EQUILIBRIUM FLUORIDES BY HIGH-RESOLUTION SOLID STATE NMR – CORRELATION OF STRUCTURAL FEATURES WITH IONIC CONDUCTIVITY

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Mixed fluorides of the compositions $Ba_{1-x}Sr_xLiF_3$ (crystallizing with inverse perovskite structure, $x \leq 0.4$) and $Ba_{1-x}Ca_xF_2$ (fluorite structure, $0 \leq x \leq 1$) have been prepared by high-energy ball milling starting from the binary source materials BaF_2, SrF_2, CaF_2, and LiF. Both the formation and decomposition processes of the mixed phases have been studied complementarily by ^{19}F magic angle spinning NMR spectroscopy as well as by ex and in situ x-ray powder diffraction. Taking advantage of spinning frequencies of up to 60 kHz enables the acquisition of well-resolved NMR spectra. In each case these clearly reveal series of F sites distinguishable by their different number of Ba^{2+} and Ca^{2+} ions in the first coordination shell. Plotting the ionic dc-conductivity of $Ba_{1-x}Ca_xF_2$ as a function of x reveals a maximum which is presumably due to the formation of these mixed sites.

A120

MECHANICAL MILLING OF MAGNESIUM BASED COMPOSITES FOR HYDROGEN STORAGE

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High-energy ball milling (HEBM) provides mechanical activation to metal hydrides to increase the rates of adsorption, desorption and chemical reactions. This is the main nanotechnology top–down approach for the synthesis of nanoparticles suitable for hydrogen storage since the applied force is sufficient to disperse the material into fine nanometric particulates or agglomerates. We have shown that HEBM of MgH_2 with additives such as metals (Fe, Co) metal oxides (VO_2,Nb_2O_5 etc), ceramics SiC,TiB_2 destroy the thin chemically passive surface coatings (e.g., surface oxides) and form fresh, clean chemically active MgH_2 surface. We have also demonstrated that such milling introduces the defects into solid compounds, which is extremely important for suitable hydrogen storage materials. Reactive milling in hydrogen atmosphere and non reactive milling in inert atmosphere to produce materials for hydrogen storage were performed.

A121

PROPERTIES OF MECHANOCHEMICALLY SYNTHESIZED Bi_2S_3 NANOPARTICLES

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The properties of mechanochemically synthesized Bi_2S_3 nanoparticles from bismuth and sulphur powder by high-energy milling in a planetary laboratory mill have been studied. XRD, specific surface area measurement, dispersion and particle size analysis, SEM, EDS, UV-VIS and DSC methods were used for the characterization of the nanoparticles. The XRD patterns confirmed the production of Bi_2S_3 (JCPDS 17-320, orthorhombic) nanopowders. Applying the Scherrer formula gives the particle size of about 24 nm for Bi_2S_3. Specific surface area increases with the increasing Bi_2S_3 production. Particles in the nanometer size range have a strong tendency to agglomerate due to their relatively large specific surface area. The average hydrodynamic diameter was shifted from 173 nm to 198 nm with the increasing milling time. SEM images reveal the product mainly consists of 1D fibre - like Bi_2S_3 structures. EDS analysis shows that the synthesized Bi_2S_3 is pure bismuth sulphide. UV-VIS spectra of the mechanochemically synthesized Bi_2S_3 nanoparticles show no absorption peaks.

Unlike more conventional methods, the controlled mechanochemical synthesis of the nanocrystalline Bi_2S_3 nanoparticles at ambient temperature and atmospheric pressure is still a great challenge.

A122

KINETICS OF MECHANOCHEMICAL REDUCTION OF SPHALERITE WITH MAGNESIUM BY HIGH-ENERGY MILLING

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The mechanochemical synthesis has attracted considerable scientific and technical interest in recent years as a consequence of the unique nanostructures and properties developed by this process. High-energy milling with a reactive metal can initiate the transformation of metal sulphides via so-called mechanochemical reduction.

The mechanochemical reduction of sphalerite with magnesium as reducing element was investigated the regard to solid-state kinetics. High-energy milling was performed in a planetary ball mill for 15-180 min. The composition and properties of the obtained powders were analyzed by XRD, specific surface area measurements and SEM. Solid-state kinetics has been evaluated based on XRD data. The process is rather straightforward with elemental zinc (JCPDS 87-0713) and magnesium sulphide (niningerite, JCPDS 01-1096) as the only solid state products. The conversion degree to Zn is 100% after 180 min. The diffusion regime is the rate-determining step for the studied system.

Mechanochemical reduction is a very straightforward, one-step, ambient temperature process without many operations. The key step is the high-energy milling which requires a suitable industrial mill for scaling up the process.

A123

MECHANOCHEMICAL SYNTHESIS OF $MoSi_2$-SiC NANOCOMPOSITE POWDER

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$MoSi_2$-25wt.%SiC nanocomposite powder was successfully synthesized by ball milling of Mo, Si and graphite elemental powders. Effect of milling time and annealing temperature were investigated. Structural and morphological evolutions were monitored by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Microstructure of powders was studied by peak profile analysis and transmission electron microscopy (TEM). Result showed that $MoSi_2$ and SiC were synthesized after 10 h of milling. Both high and low temperature polymorphs (HTP and LTP) of $MoSi_2$ were obtained in this sample. Further milling led to the transformation of LTP to HTP. On the other hands, an inverse HTP to LTP transformation took place during annealing of 20 h milled powder at 900°C. Results of peak profile analysis showed that mean grain size and strain of the 20 h milled powder are 31.8 nm and 1.19% that is in consistent with TEM image.

Keywords: $MoSi_2$-SiC; mechanochemistry; nanocomposite.

A125

MECHANICAL PROPERTIES OF WOOD FLOUR FILLED NR/CSM RUBBER COMPOSITES

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Wood flour is attractive fillers for polymers, mainly because of their low cost, low density and high-specific properties. The effect of wood flour (WF) and carbon black (CB) on rheological, mechanical and swelling properties of polyisoprene rubber/chlorosulphonated polyethylene (NR/CSM) rubber blends was investigated in the concentration range of 0 to 50 phr. The mechanical properties as well as the equilibrium swelling characteristics of the vulcanizates in toluene were measured as a function of filler loading and compared with the values obtained using commercial grade carbon black (CB). The wood flour showed good processing safety in terms of torques and scorch. For food flour filled vulcanizates, optimum tensile strength of 11MPa at 20phr was recorded. This study indicates that the potential of wood flour can be exploited further by controlling particle size and particle distribution, improving filler dispersion and also its surface functionality.

A127

SYNTHESIS AND REACTION SINTERING OF MECHANOCHEMICALLY PROCESSED YAG:Ce PRECURSOR

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Cerium doped yttrium aluminium garnet (YAG:Ce) powders are commonly used as phosphors in white light emitting diodes (LED) in order to convert the blue light from GaN diode to the yellow light and to produce the white light. The current converters utilize composite devices made of YAG:Ce phosphor powder embedded in polymer resin and suffer from low thermal stability and poor thermal conductivity. Replacement of the existing polymer-based composites by the translucent YAG:Ce ceramics could improve their efficiency, thermal stability and operating time. The present paper shows the results of mechanochemical processing of the initial powder batch on development of the phase assemblage during the subsequent thermal treatment and/or reaction sintering in temperature range of 1100-1650 °C. The latter is greatly affected by transient phase formation (monoclinic YAM and YAP with perovskite structure) accompanied by various shrinkage and expansion of crystal lattice. Moreover, addition of CeO_2 to the initial mixture requires reducing atmosphere in order to obtain Ce^{3+} ions in Y^{3+} position in the garnet crystal structure. The obtained results show that formation of the garnet structure could be moved to the temperature lower by 200 °C and formation of the side phases is avoided. On the other hand, significant evaporation of some constituents (Al, Y) was observed if the mechanochemically processed powders were heat treated in the CO atmosphere apart from Al_4C_3 precipitation. As a result the stoichiometry of YAG compound was ruined. In contrary, reaction sintering of the activated powders led to effective densification (98%) of the resultant ceramic. SEM and TEM studies show development of the microstructure during densification. The resultant ceramic was examined for thermal conductivity, optical transparency, reflection and emission under 450 nm excitation.

A128

INFLUECE OF PROCESSING METHOD ON DIELECTRIC PROPERTIES OF $BaBi_4Ti_4O_{15}$ CERAMICS

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Family of bismuth oxides was discovered more than 50 years ago by Aurivillius. Recently, there has been renewed interest in the properties of the Aurivillius phases as temperature-stable ferro-piezoelectrics. Several bismuth-layered crystal structures and their properties have been investigated in detail. However, a lot of aspects of the preparation and properties of barium bismuth titanate, $BaBi_4Ti_4O_{15}$ [BBiT] remain unexplored, whereas being promising candidate for high-temperature piezoelectric applications, memory application and ferroelectric nonvolatile memories (Fe-RAM). In present work, BBiT was prepared by solid state reaction from mixture of oxides: BaO, TiO_2 and Bi_2O_3 which was previously milled for 6 h (MA). The mixture was heated at 750 ^oC for 4 h. As a comparison, the same ceramics were prepared throught conventional solid state reaction (CSS). The same oxides mixture was homogenized for 24 h in isopropanol as a liquid medium and calcinated at 950 ^oC for 4 h which is 200 ^oC higher temperature than for MA procedure. Sintering process was carried out at 1130 ^oC for 1 h in both synthesis methods. Smaller plate like grains are noticed in BBiT ceramics prepared from powders obtained by MA process comparing to CSS process. In the temperature dependence of the dielectric permittivity, the maximum associated to the Curie temperature was higher and narrower in ceramics prepared by CSS method. Influence of the grain and grain boundaries contribution to the dielectric behaviour in both ceramics were analyzed by impedance spectroscopy.

A129

EFFECT OF SOLIDIFICATION RATE AND HEAT TREATING ON THE MICROSTRUCTURE AND TENSILE BEHAVIOR OF AN Al-Cu-Mg ALLOY

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An aluminum-copper-magnesium alloy was melt and cast in molds that promote a thermal gradient during solidification to study the effects that solidification rate exerts on the microstructure of the material. The stress-strain characteristics of heat-treated samples were related to microstructural parameters. The reactions occurring during solidification and cooling were detected and identified by means of thermal analyses. The microstructure of the material was assessed by measuring the secondary dendrite arm spacing, grain size, and porosity. It was found that these parameters increase as the solidification rate decreases. The material was heat treated to T4 and T7 conditions and tested in tension. The stress-strain curves were analyzed to determine the yield and ultimate strengths, as well as the strain to failure and that at which the ultimate strength was achieved. It was found that these properties are enhanced by microstructural refining in either testing condition. It was also found that porosity increased due to dissolution of copper-rich particles during heat treating. The best combination of strength and ductility were achieved in the T4 condition.

A130

THERMODYNAMICS OF REACTIVE DYE ADSORPTION FROM AQUEOUS SOLUTION ON THE THERMAL POWER STATION ASHES

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The values of thermodynamic parameters are the actual indicators for practical application in the adsorption process. On the basis of characteristic diagrams, the thermodynamic parameters, enthalpy and entropy of adsorption are determined, and based on those the Gibbs's free energy changes are determined. To determine the activation energy Arrhenius's plots are used. There is a negative sign of the thermodynamic parameters, in all cases. Values of activation energy indicate that the adsorption of spontaneous and easy. Entropy change (- 2.5 to – 3.9 J/K·mol) increases with increasing initial concentration of the adsorbate and decreases with increasing amount of adsorbent, suggesting that decreased disordered system at the interface of solid - solution during the adsorption of dye on the ashes. Free energy (-1.8 to 5.5 kJ/mol) decreases with the concentration of adsorbate discontinuous but continuously with increasing temperature, which is associated validity and spontaneous nature of the process. Small negative values of enthalpy change (-2.4 to – 6.6 kJ/mol), provide for the physical nature and the energy stability of the reactive dyes adsorption by ashes.

A131

MECHANOCHEMICAL SYNTHESIS OF MULTIFERROIC YTTRIUM MANGANITE

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Multiferroic yttrium manganite ($YMnO_3$) is known as a material that exhibits both ferromagnetic and ferroelectric properties making it interesting for various technological applications. In this work single-phased $YMnO_3$ was prepared for the first time by mechanochemical synthesis in a planetary ball mill. The $YMnO_3$ can be formed directly from the highly activated constituent oxides, Y_2O_3 and Mn_2O_3, after 60 min of milling time and subsequently grows during prolonged milling. The cumulative energy introduced into the system during milling for 60 min was 86 kJ/g. X-ray analysis indicates that the as-prepared samples crystallize majority with hexagonal ($P6_3cm$) and minorly with orthorhombic (*Pnma*) $YMnO_3$ structure. The morphology, structure and chemical composition of the powder were investigated by SEM with EDS and TEM. The magnetic properties of the obtained $YMnO_3$ powders were found to change as a function of milling time in a manner consistent with the variation in the nanocomposite microstructure.

A132

CATALYTIC ACTIVITY OF $La_{0.4}Sr_{0.6}FeO_3$ PEROVSKITES PREPARED VIA MECHANOCHEMICAL ROUTE IN N_2O DECOMPOSITION PROCESS VERSUS Sr-CONTAINING PRECURSOR

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Strong influence of Sr containing precursor on the phase composition and microstructure of $La_{0.4}Sr_{0.6}FeO_{3-\delta}$ perovskites prepared via mechanochemical route (mechanical treatment in APF-5 + thermal treatment at 900 ^oC) from La_2O_3, Fe_2O_3 and $SrCO_3$ (C-sample) or $Sr(NO_3)_3$ (N-sample) as well as on the oxygen mobility (SSITKA) and catalytic activity in high temperature N_2O decomposition process was revealed. The perovskite particles covered with $LaSrFeO_4$ layer structured perovskite were detected in the case of $Sr(NO_3)_3$ while two perovskites with orthorhombic and cubic structures were detected in the case of $SrCO_3$. Both samples characterized by comparable bulk oxygen mobility, while higher surface oxygen mobility was observed for N-sample. High temperature (800-900 ^oC) catalytic activity in N_2O decomposition process was higher for N-sample that correlates with surface oxygen mobility.

A133

ULTRASONIC INTENSIFICATION OF ENZYME HYDROLYSIS OF CELLULOSE

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Enzyme hydrolysis of polysaccharides in renewable lignocellulose materials has potential to develop of chemicals (sugars, extractives et al) and fuel production technologies. Slow enzyme hydrolysis reaction rate and high cost of enzyme prevent its commercial application. Mechanical activation of lignocellulose materials is a perspective method of improvement of cellulose enzyme hydrolysis. As it is known preliminary mechanical treatment of lignocellulose is ineffective activation method. So it is necessary to expose reagents to mechanical treatment simultaneously with chemical reaction. One of the ways of such chemical reaction improvement is ultrasonic treatment of reagent. Also it is well known that enzyme can be denaturated in ultrasound field, so it is impotent to study influence of ultrasound on enzyme activity.

In current research influence of preliminary ultrasonic treatment of reagents on enzyme hydrolysis of cellulose was investigated.

This work was supported by Non-commercial partnership on development of the international researches and projects in the field of energetic «Global Energy», grant MG-2011/04/6; and by Presidium Program of Russian Academy of Science “Chemical aspects of energy” 19.6.

A134

INFLUENCE OF MECHANOCHEMICAL ACTIVATION ON SINTERING OF CORDIERITE CERAMICS WITH THE PRESENCE OF Bi_2O_3 AS A FUNCTIONAL ADDITIVE

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According to its exceptional electrical characteristics, such as low temperature expansion coefficient, low dielectric constant and good mechanical properties, cordierite, $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$, represents very attractive ceramic material in the field of high temperatures. In order to accelerate the process of sintering, 1 mass% Bi_2O_3 has been added to starting mixtures. Liquid phase sintering caused by presence of bismuth-oxide leads to lowering temperature of cordierite formation. Mechanical activation of starting mixtures (0-56 minutes in vibro-mill) additionally leads to lowering sintering temperatures. Process of sintering was performed at 1200, 1300 and 1400 ^oC, for 2h. BET and PSA were employed in order to follow the changes in specific surface area and particle size of mechanically treated powders. Phase composition of starting powders and sintered materials was analyzed by X-ray diffraction method. Moreover, SEM analysis was used for analysis of powders morphology and sintered pallets microstructure.

Keywords: mechanical activation, sintering, X-ray, SEM, cordierite.

A135

RAMAN SPECTROSCOPY STUDY OF $NiFe_2O_4$ POWDERS OBTAINED BY SOFT MEHANOCHEMICAL SYNTHESIS

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The influence of milling of a mixture of $Ni(OH)_2$ and $Fe(OH)_3$ powders in a planetary ball mill on the reaction synthesis of nanosized $NiFe_2O_4$ ferrites was studied. The mechanochemical reaction leading to formation of the $NiFe_2O_4$ spinel phase was followed by XRD. The structure of the $NiFe_2O_4$ has been investigated by Raman spectroscopy. The obtained results are discussed and compared. We observed five active Raman modes. It can be concluded, that spinel phase formation was first observed after 4 h of milling and its formation was completed after 25 h. The synthesized $NiFe_2O_4$ ferrite had a nanocrystalline structure with a crystallite size of about 20 nm. This simple, low cost route should be applicable for the synthesis of other functional nanoparticles. The mechanochemical reaction was also followed by magnetization measurement at room temperature. Hysteresis loops are they typical of soft ferromagnetism.

A136

MECHANOCHEMICAL REACTIONS OF DIANTHRONIC COMPOUNDS WITH ALKALI

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Diantrones especially hypericin are components of popular antidepressants preparations. The main problem of these compounds is their low stability. The ratio of degradation of hypericin in solid plant material is significantly lower then in liquid state. Hypericin preparations were obtained by solid state mechanochemical treatment with alkali. In all cases formation of mechanocomposites takes place. The reaction of neutralization is controlled by luminescence spectroscopy method. The reaction takes place when the intensity and temperature of mechanical treatment provide plastic deformation of material. High intensity of mechanical treatment leads to fast degradation of hypericin. The low temperature leads to brittle failure of material and production of high dispersed mechanocomposite without reaction. The increasing of temperature leads to plastic deformation of material, reaction between hypericin and alkali and decreasing of dispersity of material. The optimal conditions are stated out.

A137

ASYMMETRIC ORGANOCATALYSIS IN A BALL MILL

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Enantioselective C-C-bond formations have been achieved by asymmetric organocatalysis in a ball mill. Alkaloids and proline served as chiral catalysts providing products with high enantioselectivities. Commonly, the reactions were performed solvent-free. With a scalemic catalyst, non-linear effects have been observed.

A138

INFLUENCE OF HIGH-ENERGY BALL-MILLING ON PHASE TRANSFORMATIONS AND STRUCTURAL, SURFACE AND PHOTOCATALYTIC PROPERTIES OF TITANIA

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The photocatalytic activity of nanocrystalline anatase TiO_2 P25 powders ground at high-energy, as measured by the degradation of gaseous nitrogen oxides and of salicylic acid, decreases with milling time. The origin of this decrease was sought in the changes of the starting anatase induced by grinding. Firstly, high-energy ball-milling induces phase transformations of anatase TiO_2. Anatase transforms into rutile via the intermediate TiO_2-II form, a phase which forms in equilibrium conditions at high pressure and high temperature. These phase transformations, which are induced mechanically, were followed by X-ray diffraction and were concluded to be uncorrelated with the loss of photocatalytic activity. The surface states of titania particles were studied by several analytical methods which probe different physico-chemical characteristics. All results converge to conclude that grinding increases the density and the reactivity of active surface groups. These groups are identified as high-affinity sites by low-pressure N_2 adsorption, as protolytic hydroxyls by potentiometric titration, and as radiative states by photoluminescent experiments. However, the increase in the density of surface sites is due to a relaxation of the outermost atomic layers which, according to the grinding time, results in poorly crystallized superficial zones of monocrystalline particles, as observed by TEM, and in gas and proton adsorption sites with a broadened energy distribution. Finally, the photoluminescence experiments show that grinding affects the recombination of photo-generated electrons and holes.

A139

CATALYST COMPONENT INTERACTIONS IN ZINC ALUMINATE SPINEL CATALYST

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The only industrial process (Esterfip-H) which applies heterogeneous catalyst for biodiesel production applies a zinc aluminate spinel catalyst. Zinc aluminate spinel, ($ZnAl_2O_4$), in combination with copper can appear also in low-pressure methanol and in low-temperature shift catalyst. Bulk and monodispersed $ZnAl_2O_4$ can be synthesized via solid-state reaction of zinc and aluminum oxides above 800°C, or via wet chemical routes. In this work two series of $ZnAl_2O_4$ were prepared: *a)* by mechanical powder mixing of catalyst components (ZnO and alumina of different origin) and *b)* by impregnation of different alumina or their precursors by zinc nitrate water solution. All of used alumina or their precursors (gibbsite, boehmite, γ-Al_2O_3 and α-Al_2O_3, fraction below 63 μm) were synthesized in our Laboratory. *a)* The metal oxide powders in eqiumolar ratio were homogenized in a rotational mixer with 30 rpm during one hour. Pure components, as well as their mixtures were heated at 350°C, for 4 hours and later at 950°C for 1,3,5,7 and 10 hours in air. *b)* The impregnated samples were subsequently dried at 105°C for 12 hours, after that calcined at 350°C for 4 hours and thermally treated as the samples *a)*. The intensity of catalyst component interactions, CCI, was studied by XRD and by measuring of specific surface area (SSA, BET by LTNA) of the prepared samples. The intensity of CCI, which precedes sintering or takes place simultaneously, was defined as a ratio, Q of the theoretical value of SSA (defined as sum of partial surface areas of the system components) and the experimentally measured surface area of the synthesized systems. In absence of CCI this ratio should be equal to one. The XRD results show that the formation of $ZnAl_2O_4$ is more complete in the system which was prepared by impregnation. The creation of $ZnAl_2O_4$ was very slow in both systems on α-Al_2O_3. That could be explained by compact structure of α-Al_2O_3, compared to other aluminum compounds (SEM images). The reaction between the components was not fully completed. Traces of unreacted ZnO were recorded in all of samples by XRD. The intensity of CCI is considerably higher in the system that was prepared by impregnation. For example, the Q ratio in samples ZnO-Gibbsite, ZnO-Boehmite prepared by impregnation (treated for 10 hours) was 2.93 and 5.40 and for the corresponding samples that were prepared by mechanical mixing of metal oxides these values were 2.15 and 3.69, respectively. When the samples were prepared on γ-Al_2O_3 these differences practically disappear. These results testify the great influence of delivered water from hydroxide and oxyhydroxide to the degree of sintering and to the rate of $ZnAl_2O_4$ formation. Samples prepared on α-Al_2O_3 have too small SSA, and therefore the used device for SSA measurement did not give reliable results.

Acknowledgement: This work was supported by the Serbian Ministry of S & TD (OI-172059) and Provincial SS&TD (Grant: 140-474-4246).

A140

THE EFFECT OF HIGH-ENERGY MILLING ON THE REACTION SINTERING OF SILICON NITRIDE CERAMICS

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Silicon nitride ceramics offer attractive mechanical properties at room and elevated temperature, good chemical stability but manufacturing cost effective products still remains the open question. The main reason lies in the reactive sintering essential for crystallization of the elongated β-Si_3N_4 needles, necessary for toughing mechanism of the resultant ceramics. Thus temperature over 1800 °C and the relevant gas pressure sintering is crucial for formation of a desired microstructure. The parallel solution for making high strength silicon nitride ceramics could be maintaining their nanostructure from the relevant powders. In the present paper nanostructured silicon nitride and aluminium nitride powder mixtures have been successfully produced by high-energy mechanical activation in the planetary mill. The resultant powder showed higher ability for densification at lower temperature (1600 °C) in comparison to the reference samples. This paper describes the effects of high-energy milling and a subsequent precursor powder processing on ability for densification and β-sialon solid solution formation. The effect of planetary milling parameters (time, size of grinding ball, ball-to-powder ratio, surfactants addition) and means of deagglomeration by the ultrasound disintegration (type and quantity of dispersant, frequency and time of the ultrasonic action) were studied. The resultant powders were examined by SEM and TEM as well as the specific surface area (BET) was measured and grain size distribution was analyzed. The mean particle size from different methods was calculated and compared. It has been found that significant agglomeration occurred in the samples milled with the highest energy. The results show the crucial effect of dispersant presence and its behavior during mechanical activation on the resultant particle size distribution and ability for densification.

A141

THE MECHANOCHEMICAL TREATMENT OF $V_2O_5/(NH_4)_2Mo_2O_7$ MIXTURE

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The mechanochemical treatment of $V_2O_5/(NH_4)_2Mo_2O_7$ (ADM) mixture was studied for the first time. It was found that dry treatment brings about partial decomposition of ADM with formation of Mo_9O_{26} without changes in V_2O_5 phase. The milling in ethanol leads to formation of Mo_9O_{26} and $MoO_{2.8}$ phases as well as to anisotropic deformation of V_2O_5 with increase of basal plane content. The milling in water causes two types of changes. At the short-time treatment the formation of Mo_9O_{26}, $MoO_{2.8}$, χ-Mo_8O_{23} and $V_2O_5{\cdot}nH_2O$ took place. The elongation of milling time leads to reaction between $V_2O_5{\cdot}nH_2O$ and NH_3 with formation of $(NH_4)_2V_6O_{16}{\cdot}2H_2O$ and hydration of molybdenum suboxides to $HMoO_3{\cdot}2H_2O$. It was found that the samples containing molybdenum suboxide mixture and $V_2O_5{\cdot}nH_2O$ show high selectivity to propylene in oxidative dehydrogenation of propane.

A142

SPECTRAL AND MECHANICAL PROPERTIES OF THE MATERIALS STRUCTURED WITH CARBON NANOTUBES

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Carbon nanotubes are considered as the good candidate to modify the surface properties of the organic and inorganic structures. Both the spectral and mechanical properties as well as quantum chemical simulation are discussed to explain the increase in transmission and hardness of the nanostructured polyvinyl alcohol films, magnesium fluoride, etc. The basic features of carbon nanotubes are regarded to their small refractive index, strong hardness of C—C bonds as well as complicated and unique mechanisms of charge carrier moving. The structures of the composite films and their mechanical properties are modeled too. The peculiarities of new nanostructured materials and their possible optoelectronics and display applications will be under consideration. The results have been supported by RFBR grant #10-03-00916 and RAS Presidium Program # 21.

A143

CHITOSAN/POLYESTER MATERIALS OBTAINED IN SOLID STATE

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The novel approach to modification of the polymers in simple one-step procedure under conditions of shear deformation and pressure (a twin-screw extruder) - Solid-State Reactive Blending (SSRB) - was employed to obtain nanostructured materials based on chitosan and PLLA or PLGA. The entire modification process proceeds in the solid state (below melt temperature of the components) without any solvents and catalysts. Strong interaction of the components in the blends during co-extrusion has resulted in facilitating a degree of particle dispersability. The new materials demonstrate amphiphilic behaviour with a propensity to disperse in organic solvents on colloidal level (a mean particle size of 200-400 nm). They were used for preparation of films, microparticles, microfibers, and were demonstrated to be very promising materials for biomedical applications.

A145

STEPS OF FINE GRINDING OF RICE HUSK AND CEREAL STRAW

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A mechanism of comminution and fine grinding of plant materials have been investigated. In case of rice husk and cereal straw we have found that comminution proceeds in stages. At the beginning the plant separates into tissues, and then these tissues are grinded apart. Last stage involves destruction of plant cells. This order is not absolute; the grinding of tissues may take place simultaneously with cell crush and depends on conditions of mechanical treatment. It was found that composition and even genotype of plants influence on their mechanical properties and grinding process. The methods of fine and effective grinding of plant materials and agriculture wastes without increase expenditure of energy are also discussed.

A146

RAPID MECHANO-CHEMICAL REACTIONS DURING ELECTRIC DISCHARGE ASSISTED MECHANICAL MILLING

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Advanced materials manufacturing methods require clean non-polution process, high speed and precise process, mechano-chemically integrated process, and highly reliable final products. Many functional materials are traditionally synthesized by slow reaction processes that are energy and time consuming. In the present world there is strong demand on development of modern materials and materials processing methods that could offer rapid reaction rates, energy efficiency and be environmentally safe.

Electric discharge assisted mechanical milling (EDAMM) is a new and exciting materials processing technique which combines the attributes of conventional mechanical milling with all effects generated by electric discharges. It is demonstrated that EDAMM can be used to synthesize a range of functional materials in a matter of minutes, rather than days.

This presentation provides an overview of recent development of EDAMM method and its application in rapid materials processing and synthesis of functional materials and their applications.

In this report, it will be demonstrated the versatility of EDAMM by:

i) synthesis of functional hard materials: In this study, synthesis of ultra-hard metals from elemental powders by electric discharge assisted mechanical milling technique was investigated. The technique has the following advantages: rapid reaction rate, controlled reaction, direct reaction between elements without adding other elements into the system and cost effectiveness;

ii) synthesis of functional oxides used in electronic, optical applications and super-capacitors based energy storages: By using EDAMM to synthesize these materials, high purity phases can be formed in around 1% of the heating time, when compared to conventional solid-state synthesis;

iii) rapid reduction reactions and extraction of metals from oxides,

iv) synthesis of metal hydrides for hydrogen storage applications,

v) synthesis of exotic crystallographic structures such as porous silicon for battery applications.

A147

MECHANOCHEMICAL SYNTHESIS AND PROPERTIES OF SUPRAMOLECULAR DRUG COMPOSITIONS

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The formation of supramolecular structures with various degrees of orderliness results in reorganization of weak intermolecular interactions due to varies a relative positioning of molecules. We have investigated this phenomenon in the mixtures of low-weight molecular organic compounds (the medicinal substances) taken as substrates, and natural polymers (poly-carbohydrates of various molecular weight and glycyrrhizic acid) as receptors. One of the main curiosities of complexation is increasing in solubility of very low soluble drugs in water up to 100 times. It was demonstrated that mechanochemically prepared water-soluble complexes can be used as effective drug delivery systems for a number of anti-coagulating, cardio active, psychotropic, analgesic and the anti-inflammatory drugs. In toxic-pharmacological tests the possibility of multiple decreases in therapeutic doses was shown with preservation of base pharmacological activity and decrease side effects.

A148

MECHANOCHEMICAL DESTRUCTION OF WATER-SOLUBLE POLYSACCHARIDES

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In the present work we investigated the influence of mechanochemical treatment on molecular - mass characteristics of water-soluble polysaccharides used in pharmaceutical and the food-production industry - Arabinogalactan from a Larches, Fibregam - glycoprotein from an Acacia, Hydroxiethylstarch (200/0,5) and Dextranes 10, 40, 70. It has been applied “intensive” mechanochemical treatment - in planetary mill (40g), as far as "soft" - in a rolling ball mill (1g). At use of an intensive mechanochemical treatment - there is a significant decrease in molecular weights of polysaccharides. In “soft” mechanical conditions it is possible to avoid significant changes in the molecular-mass characteristics of polymeric materials. In any cases the polymers with higher molecular weight are more sensitive for mechanochemical destruction.

A149

MECHANOCHEMICALLY-ASSISTED SYNTHESIS AND CHARACTERIZATION OF Zr-DOPED HYDROXYAPATITE NANOPOWDERS

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Hydroxyapatite (HAp) bioceramics attract researches' interests over the decades as a candidate for ideal bone tissue reconstruction material. Its excellent biocompatibility and bioactivity, originating from chemical similarity to the mineral part of the bones, make this material perennial fountain of inspiration and application of wide range of experimental approaches to improve its properties, mainly that of mechanical nature. Doping the crystal lattice of HAp with various ions, while preserving pure apatite crystal structure, seems promising way for alteration of its biological and mechanical properties.

This study deals with mechanochemically-assisted synthesis of Zr-doped HAp with different amounts of Zr ions. Reactants mixture was activated in a planetary ball mill using a wessels and balls made of zirconia. The frequency of the rotation of wessels around the common axis was 260 revolutions per minute, reaction time was 3 h.

The influence of mechanical treatment on final phase purity, chemical composition, morphology and particle size was investigated. The comparison of incorporation efficiency between mechanochemical treatments and pure chemical precipitation is made.

A150

THE MORPHOLOGY, STRUCTURE AND LUMINESCENT PROPERTIES OF Gd_2O_3:Eu SYNTHESIZED BY AEROSOL ROUTE AND HIGH ENERGY BALL MILLING

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The processing of europium-doped gadolinia (Gd_2O_3:Eu) nanostructured particles has been realized using the bottom-up chemical approaches either by a hot-wall spray pyrolysis technique (SP), starting from the aerosol of common nitrates precursors, or a high energy ball milling (HEBM) of acetate precursors. The former one yields high-purity nanostructured non-agglomerated particles having spherical morphology and high chemical homogeneity. The HEBM-derived particles are with irregular morphology, submicronic in size, having an amorphous structure after 12h of milling. The detailed study of the crystalline structure and luminescent properties were proceeded for the different europium concentrations (1, 2 and 6at%) by means of XRPD, SEM, DSC, FTIR and steady state-fluorescent spectroscopy. The phase development and structural changes, followed by Fullprof program, implied the nanocrystalline inner structure (crystallites < 20 nm) and the coexistence of the following crystal phases for as-synthesized SP samples: two cubic phases, having either a bcc (SG: *Ia3*) or a fcc (SG: *Fm-3m*) structure, and a monoclinic phase with the space group (SG) *C2/m*. In the cubic *Ia3* phase the cell parameter was affected by the europium concentration and the thermal treatment temperature, followed with progressive increase in crystallite size. On the other side, the monoclinic phase concentration decreased after additional thermal treatments. Luminescence measurements have detected the presence of divalent europium near to 480 nm, aside to the typical trivalent europium spectra. This behavior could explain the increase in the emission intensity in the blue spectral region due to the divalent europium.

A152

THE PROPERTIES OF THE COMPOSITES SUPPORTED ON STAINLESS STEEL FOIL BY LOW TEMPERATURE IMPLANTATION METHOD

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The low temperature implantation method (low temperature plasma and ion-stimulated modification) was used for the preparation of nano- and micro-layer of different elements (Al, Ni, Cr, Ti, Mo, Hf, Pd) or layer by layer covers from different elements (for example, Ni/Al, Ni/Al/SS) on surface of stainless steel (SS) 12Cr18Ni10Ti foil (the thickness 80 μm). The synthesized samples were studied by means of XRD, XPS, SEM and AFM methods. The high catalytic activity and stability of the properties in reactions of CO and CH_4 total oxidation and high selectivity in hydrogen production from ethanol were established.

A153

MECHANOCHEMISTRY OF COMPLEX OXIDES

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Mechanochemistry has a long history and it continues to be of high importance. In the present contribution, selected examples are presented of homogeneous and heterogeneous mechanochemical reactions leading to *complex nanooxides* with a nonequilibrium structure and unique functional properties. The results of the systematic Mössbauer, NMR, neutron diffraction, XRD, HRTEM, XPS, Raman, and SQUID studies of these nanomaterials are presented. Quantitative microstructural information on the nonequilibrium cation distribution, the noncollinear spin arrangement, the alteration of the nearest neighbor configuration, and the deformation of the polyhedron geometry in the nanostructured oxides is provided. In addition to the results of structural studies, an extraordinarily high reactivity of mechanosynthesized oxide nanoparticles is demonstrated. The macroscopic behavior of mechanosynthesized nanooxides is discussed in terms of structural effects in the near-surface layers of oxide nanoparticles. The work is supported by the DFG in the framework of the Priority Program "*Crystalline Nonequilibrium Phases*" (SPP 1415) and by the VEGA (2/0174/11).

A154

MECHANOCHEMISTRY AND DEVELOPING NEW SOLID FORMS OF PHARMACEUTICAL MATERIALS

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The delivery of new drugs to market requires an understanding of how factors such as polymorphism, crystal morphology, solubility can affect the development process. Solubility and other properties are frequently altered by the formation of salts rather than by use of the pure drug alone. For some molecules, however, this presents problems when there are few, if any, possible ionisation sites. In recent years, therefore, there has been an interest in the use of multicomponent crystals (also known as cocrystals) as new forms of the molecule and in which the molecule remains in a neutral state. One consequence is that this introduces the possibility of using a wide range of potential components to add to the system during crystallization. Mechanochemistry (i.e. in this case the mixing of two or more solid organic materials together to form a single crystalline multicomponent phase) has been an important development in screening for alternate forms of a drug molecule. My lecture will introduce some of the issues behind pharmaceutical solid form development and how mechanochemistry has allowed for a rapid and effective way of screening for possible combinations of molecules to form cocrystals.

A155

FORMATION OF NANOCRYSTALLINE AND AMORPHOUS PHASES IN COMPLEX METALLIC ALLOYS DURING HIGH ENERGY MECHANICAL MILLING

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It is known that non-equilibrium processing techniques can be exploited to generate novel materials with suitable crystal structures and microstructures for various technological applications. There are intense activities to understand the origin and role of complex metallic alloys (CMAs) phases for developing advanced materials while experimenting with the various non-equilibrium processing techniques. Among the non-equilibrium techniques developed during the past few decades to synthesize novel materials include rapid solidification processing (RSP), mechanical alloying/ milling (MA/MM), plasma processing, vapor deposition, ion or electron or neutron irradiation, severe plastic deformation etc. Mechanical alloying which is a solid state powder processing technique involving repeated cold welding, mechanically activated interdiffusion, fragmentation and dynamic recrystallization of powder particles in a high energy ball mill is an ideal processing route to develop nanocrystalline materials at ambient temperature. In the recent years it is shown that mechanical alloying/milling can convert an intermetallic compound or elemental powder blend into nanocrystalline or amorphous aggregate. One of the advantages of this conversion to nanocrystalline or amorphous state is the enhancement of ductility and toughness. The aim of the present work is to investigate the evolution of metastable phases and microstructures as well as some properties of Al-based and Mg-based CMAs processed through mechanical milling and rapid solidification techniques. The suitable annealing treatment is given to investigate the thermal stability of those phases. The milling is carried out in a planetary/attritor mill at various milling intensity with varying the ball to powder ratio in a suitable milling medium. The milled and the annealed samples are characterized with the help of XRD, SEM and TEM. It is found that these alloys can give rise to the formation of nanocrystalline phases of grain sizes to a certain minimum value. At present it is not clear why, given a milling energy, some alloy systems restrict to the formation of nanograin of a particular size and do not lead to the formation of amorphous phase. The relative stability criteria will be discussed based on the modified Miedema model of free energy including the contribution from grain size effects and the lattice strains generated during milling. Attempts will be made to prepare the compacted and sintered sample from the milled powders. The mechanical properties of the compacted and the RSP samples will be evaluated using the indentation techniques. Efforts will be made to establish the possible structure-properties correlation in these novel complex metallic alloys containing the metastable phases.

A156

ANALYSIS OF STRUCTURAL CHANGES OF MECHANICALLY ACTIVATED CHALCOPYRITE CONCENTRATE AND MANGANESE DIOXIDE MIXTURE WITH THE HELP OF A SINGLE DIMENSIONLESS NUMBER

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In an attempt to improve the dissolution rate of a chalcopyrite concentrate in the presence of manganese dioxide as the oxidant, a research study on the pre-leaching mechanical activation treatment of the mixture has been carried out. In this paper, we focus on the structural changes of the feed material induced by various milling conditions using XRD analysis. The influence of the essential milling parameters, *i.e.* charge ratio, milling speed and milling time has been collectively examined with the aid of a dimensionless activation number. It was observed that the phase composition of chalcopyrite sample did not undergo any sensible changes with an increase in activation number while manganese dioxide was progressively decomposed to lower oxides. The evolution of crystallite size and micro-strain of both chalcopyrite and manganese dioxide could be correlated well with the activation number. It was concluded that activation number may potentially be useful in prediction and modeling of mechanical activation of mineral particles.

A157

ALUMINIUM BASED NANOCOMPOSITES PRODUCED BY BALL MILLING AND HOT EXTRUSION

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Al-based composites are among new industrial materials, which were developed in order to reduce the weight of vehicles in the aerospace industry. Quite recently, they have found application in the automobile industry due to a high specific strength combined with high wear resistance. Boron carbide or nitride containing composites may be applied both as wear resistance and radiation-protective materials. In our work we investigated composites based on structural Al alloys, filled with boron carbide (or nitride) and nanosized tungsten. Initial components were milled together in water-cooled planetary ball mill. No interaction between components was observed in the as-milled samples. The powder mixture was preliminarily degasified at 400 ^{o}C for 5 h and, then, subjected to hot extrusion in aluminum bar at 450 ^{o}C with a relative reduction of 10:1 and an extrusion rate of 0.5 m/min. Hot extrusion gave a band of composite material 1.1x5x100 cm^3. Scanning electron microscopy of extruded samples shows the uniform distribution of fillers in the matrix. A cross-section of samples show that there were not any defects like porosity and cracks, which could form during the composite fabrication due to difference between the thermal expansion coefficients of aluminum matrix and filler. The X-ray diffraction analysis after hot extrusion showed that the same phases were present in as-milled composite; the changes in lattice parameters values were within experimental error. Grain size for Al-based solution increased from 35 to 90 nm after hot extrusion. Compression tests shows that the material deformed elastically up to relative strain of approximately 5%, at higher relative strain, the material passed into the elastic-ductile zone until reaching maximum strength, which was 560 MPa at a strain of 11%. At a strain of 14% and stress of 450 MPa, the material became unstable and its brittle failure was observed. The compressive modulus of elasticity was 9.5 GPa. Tension tests indicate that samples can be deformed elastically up to the failure. The tensile strength was 195 MPa at a strain of 5%. The tension modulus of elasticity was 9.5 GPa. Wear test suggest that the mechanism of friction interaction and wear of Al-alloy matrix and composite is mainly the deformation nature of the fracture. In the case of composite, this mechanism is characterized by destruction of the surface layers (linear wear of 6.4 µm). The Al-alloy matrix has destruction in the deeper layers and has the linear wear 55.3 µm. It was shown that friction coefficient is by almost two times lower and the wear spot is by almost 5 times smaller that those for the pure matrix material. . This work is supported in the frame of federal target program «Scientific and scientific-pedagogical personnel of innovative Russia», state contract P1578.

A158

MECHANOCHEMICAL LEACHING OF SPHALERITE IN AN ALKALINE SOLUTION

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This study investigates the effect of using mechanical activation on the extraction of zinc from sphalerite in an alkaline solution containing lead carbonate. The combined mechanical activation and chemical leaching in a single operation (mechanochemical leaching) is found to be more effective in comparison with the separate mechanical activation and subsequent chemical leaching. A novel hydrometallurgical process for recovering Zn from sphalerite in alkaline solution via chemical conversion with $PbCO_3$ was developed in this work. In the stirred ball mill, the S originally present in sphalerite can be converted into PbS, while the Zn can be converted into $Na_2Zn(OH)_4$ in the alkaline solution in presence of $PbCO_3$. And then, the Pb in PbS deposited in the leach residues can be converted into $PbCO_3$ again in the Na_2CO_3 solution. It was found that over 86% of Zn can be extracted from sphalerite when the leaching process is operated in 6 mol/L NaOH solution at 90 °C with $PbCO_3$ as additive, and stainless steel ball of 5 mm diameter as activation medium, the mass ratio of ball to raw materials of 30:1, Pb/ZnS of 0.9:1.

Keywords: Sphalerite; Alkaline leaching; Mechanochemical leaching; Lead carbonate

A159

ANTIMICROBIAL ACTIVITY OF PALLADIUM(II) COMPLEXES WITH *O,O'*-DIALKYL ESTERS OF (*S,S*)-ETHYLENEDIAMINE-*N,N'*-DI-2-(4-METHYL)-PENTANOIC ACID

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Numerous complexes based on palladium(II) ion have been synthesized and their different biological activities have been documented. The impact of different palladium complexes on the growth and metabolism of various groups of microorganisms has been studied.

This study is focused on the *in vitro* antimicrobial activity of four bidentate *N,N'* - ligand precursors, including *O,O'* - dialkyl esters (alkyl = ethyl, *n*-propyl, *n*-butyl and *n*-pentyl), and the corresponding palladium(II) complexes against 15 species of bacteria and fungi is investigated. Testing is preformed by microdilution method and minimum inhibitory concentration (MIC) and minimum microbicidal concentration (MMC) have been determined.

A160

STRUCTURE FORMATION IN ULTRA IGH MOLECULAR WEIGHT POLYETHELENE AT MILLING TOGETHER WITH ULTRA FINE TUNGSTEN

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Polymer composites attract significant attention due to their high functional properties and low density. Ultra High Molecular Weight Polyethylene (UHMWPE) is unique polymer material, which combines high mechanical properties, low friction coefficient and good wear resistance. Further improvement of UHMWPE properties can be achieved by filling of various type of reinforces. However, in contrast to other thermoplastics, UHMWPE at melting temperature transforms not to liquid state, but into high viscosity substance. Because of that, the distribution of powder fillers in the polymer matrix by mixing in liquid state for UHMWPE is nearly impossible. In our study, high-energy ball milling was used in order to form well-homogenized composites. Ultra fine tungsten powder was used as filler for polymer matrix. Structure of obtained composites was studied using scanning electron microscopy and X-ray diffraction. If was observed that structure of polymer matrix composites significantly depends on the milling conditions. Scheme of structure formation the composite during mechanical mixing was proposed. Mechanical and tribologic tests show a negative effect of irregular distribution of fillers particles on the mechanical and functional properties of the composites.

A161

MECHANOCHEMISTRY IN MATERIALS PREPARATION

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Mechanochemistry is closely associated with materials science. Now it is evident that both mechanical activation and mechanical synthesis may help to solve difficult problems of preparation not only composite materials but also single phase complex oxide compounds and some metallic alloys. Institute of Solid State Chemistry and Mechanochemistry has a good experience in mechanochemical applications for materials preparation. In this presentation some results of a recent activity of the Institute will be summarized to demonstrate the efficiency of mechanochemical approach:

- nanoceramics synthesis and sintering;
- intermetallic compounds and nano-composites;
- drug delivery systems;
- bioactive surface composites and bio-ceramics, etc.

Mechanochemistry is rather attractive from ecological point of view but full scale technological realization of mechanochemistry is strictly dependent on efficient and long life mills which are not available in the market till now.

A162

INVESTIGATION OF COVALENT BONDS USING AFM-BASED SINGLE-MOLECULE TECHNIQUES

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The mechanical degradation of macroscopic polymeric materials is directly related to the rupture of individual chemical bonds, which determine the properties of synthetic and natural materials. To obtain a deeper understanding of material failure it is essential to understand the breakdown of individual chemical bonds. With the help of AFM-based single-molecule force spectroscopy (SMFS), i.e. dynamic SMFS and force clamp SMFS, the kinetic parameters governing bond scission become experimentally accessible.

To perform experiments using SMFS, the AFM tip, which is functionalized with chemically active groups, is moved towards the substrate surface, where individual molecules are anchored. By picking up an individual molecule and increasing the distance between AFM tip and substrate surface, a tensile force is applied to the molecular chain providing information about the elastic properties of the investigated molecule.

In the well established dynamic SMFS mode, the distance between AFM tip and substrate is increased until the tensile force exceeds the strength of the weakest bond in the tethered molecule. From the measured force-extension curve the bond rupture force can be extracted as a function of the force-loading rate.

A more recent approach is the force clamp technique, where an individually coupled molecule is stretched up to a defined force, and retained at this force until a spontaneous bond scission occurs. The recorded force versus time plot yields the bond lifetime as a function of the clamp force.

Here, we report the results from temperature-dependent experiments using both, dynamic SMFS and force clamp SMFS, where single molecules of carboxymethylated amylose were covalently tethered between a silanized glass substrate and a silanized silicon nitride AFM tip via amide as well as ester bonds at neutral pH and acidic pH, respectively.

In order to extract the kinetic and structural parameters, data sets were analyzed with two alternative Arrhenius kinetics models using a global fitting procedure based on the maximum likelihood method. The obtained results indicate that force clamp SMFS experiments are much better suited for quantitative work than dynamic SMFS experiments.

A163

NMR STUDIES IN MECHANOCHEMISTRY

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We report on the application of various NMR techniques to the study of ion dynamics and local structure in materials prepared by mechanochemical processes, both homogeneous and inhomogeneous ones. High-energy milling has been used for (i) the reduction of the crystallite size of monophase materials to the nanometer scale, (ii) the change of local structure and redistribution of ions, and (iii) the synthesis of stable or metastable compounds. In particular, in nanocrystalline Li as well as F ion conductors, being characterized by a large fraction of grain boundaries, NMR lineshape and spin-lattice relaxation measurements allowed us to measure the often very fast diffusivity as compared to that of the corresponding unground samples. Magic angle spinning (MAS) and static NMR spectra were intensively used to investigate the ion redistribution and microstructural disorder of mechanically treated samples as well as to trace the mechanosynthesis of new fluorides and oxides.

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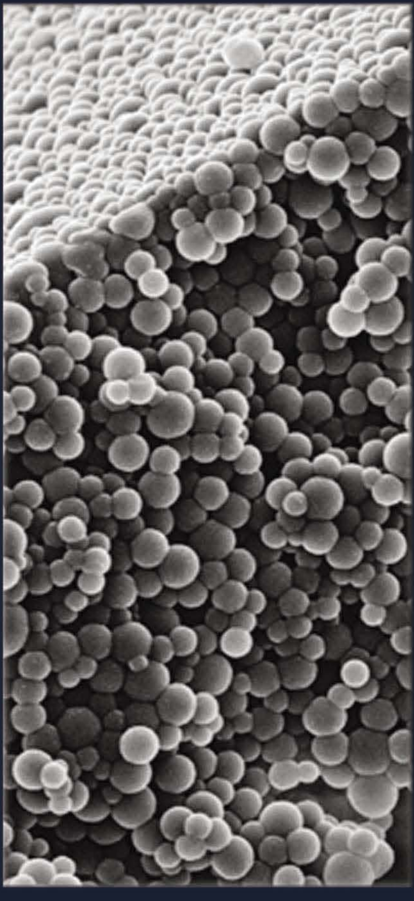

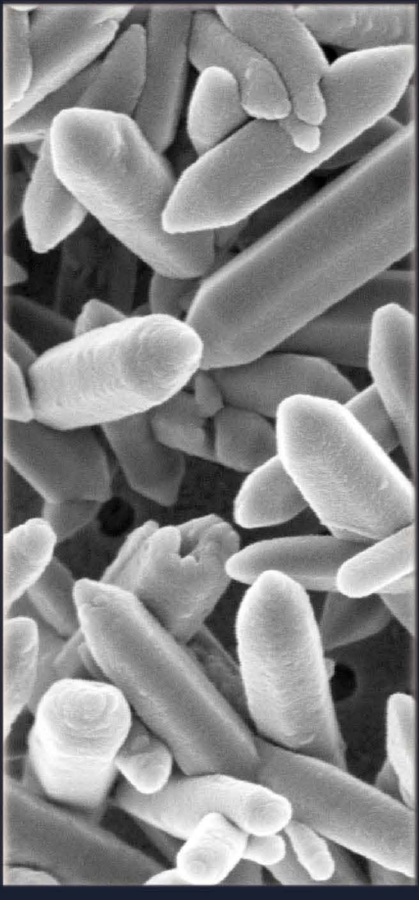

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