



**RESEAU FRANÇAIS DE  
MECANOSYNTHESE**

**Lettre N°79**

**Octobre 2001**

**185 Groupes de Recherche  
(dont 111 à l'étranger / 33 Pays)**

**Bureau du RFM : E. Gaffet (Président)  
G. Le Caër (Secr. Gén.), A.R. Yavari (Trés.)**

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Rubrique Pages Sciences et Techniques pour l'Ingénieur (Rubrique Sciences)  
vous y trouverez les anciennes lettres du RFM (accessible par Adobe Acrobat)  
les statuts du RFM ainsi que les annonces concernant les JRFM'2001 et quelques éléments mis à jour  
régulièrement concernant les derniers résultats dans ce domaine.

200  
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Les JRFM'2002 seront intégrées dans le cadre du Congrès  
**Matériaux 2002**

(Tours – France, du 21 au 25 Octobre 2002)

Symposium 1 :

**Poudres et Matériaux Nanostructurés,  
du fondamental aux applications industrielles**

Website : <http://www.materiaux2002.net>

E\_mail : [materiaux@materiaux2002.net](mailto:materiaux@materiaux2002.net)

**Attention :**

la date limite pour les propositions de communications  
est le 9 Novembre 2001

**Sommaire**

⇒ Thèses / Congrès

⇒ International Conference "Fundamental Bases of Mechanochemical Technologies"

• Novosibirsk, August 2001 / Liste des contributions (résumés)

⇒ Bibliographie du mois de Septembre

⇒ Dossiers d'annonces techniques

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## Congress and School Announcements

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### (IWSIS-3)

October, 7-12, 2001.

3rd International Workshop on Surface and Interface Segregation , Island of Porquerolles, French Riviera,  
This Workshop is devoted to the study of the segregation phenomenon  
in defects of crystallized solids (surface, grain boundary, interface of  
interphase...)

INFOS, : <http://www.crmc2.univ-mrs.fr/confs/iwsis>

### "VI International Symposium on Self-Propagating High-Temperature Synthesis, (SHS-2001)"

Haifa, Israel . October 14-18, 2001.

More information on the

Web site: <http://www.technion.ac.il/technion/materials>

### Nano 2002

16 - 21 Juin 2002

Orlando, Florida - USA

Website : <http://www.nano2002.com/>

### Workshops

#### Gordon Research Conference on Granular and Granular-Fluid Flow

Plymouth, NH, USA June 30 - July 5 ,2002

<http://sol.rutgers.edu/~shinbrot/gordon2002/gordon2002.html>

### RQ11

Rapidly Quenched and Metastable Materials

25-30 August 2002

Department of Materials, University of Oxford, UK

Contact: RQ11 Conference Organiser, Beggars Roost, Channels End Road,  
Comworth Bedford MK44 2NS, U.K.

Tel: +44 (0) 1234 378862

Fax: +44 (0) 1234 376219

E-mail: [mailto:rq11@materials.ox.ac.uk](mailto:mailto:rq11@materials.ox.ac.uk)

Website: <http://www.materials.ox.ac.uk/rq11>

### 10th European Symposium on Comminution

Heidelberg from 2-5 September 2002.

Org. European Federation of Chemical Engineering

Full information available at <http://www.comminution2002.de>

L. A. C. A. M. E – 2. 0. 0. 2

EIGHTH LATIN AMERICAN CONFERENCE  
ON APPLICATIONS OF THE MÖSSBAUER EFFECT  
PANAMA, 22-27, SEPTEMBER, 2002.

E-mail: [mailto:lacame2000@fisica.ciens.ucv.ve](mailto:mailto:lacame2000@fisica.ciens.ucv.ve)

<http://www.up.ac.pa/Eventos/lacame2002/inicio.htm>

### Matériaux 2002

Tours - France

21- 25 Octobre 2002

Website : <http://www.materiaux2002.net>

E\_mail : [materiaux@materiaux2002.net](mailto:materiaux@materiaux2002.net)

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**SOUTENANCES DE THESE**  
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**Sébastien Lehnard**

**"Texture, Microstructure et Propriétés d'un Alliage Fe-40 Al à grains fins  
obtenu par métallurgie des poudres et extrusion :  
Influence des paramètres du procédé et de traitements thermiques"**

**Université de Metz - 5 octobre 2001-08-23**

**Jury :**

R. Schwarzer (Rapp.), E. Gaffet (Rapp.), JP Morniroli, V Skrotzi, R. Baccino, A. Hazotte,  
F. Wagner (Dir. Thèse), Th. Grosdidier (Co. Dir. Thèse)

**Abstract**

**Version Française**

Les intermétalliques Fe 40 %at. Al, de structure B<sub>2</sub>, ont suscité un intérêt accru au cours de la dernière décennie. Leur élaboration par mécanosynthèse, permettant le renforcement par une dispersion fine d'oxyde d'yttrium, et extrusion a ouvert une voie pour remédier aux problèmes liés à leur fragilité et à leur faible ductilité. L'étude présentée dans ce document s'attache tout d'abord à caractériser l'influence de certains paramètres du procédé d'élaboration sur l'évolution des microstructures, des textures et des propriétés mécaniques de barres extrudées. Pour cela, la température d'extrusion (1000 à 1250°C) et le rapport d'extrusion ont été modifiés. Des poudres de natures différentes, contenant 15 % de poudres non broyées, ont été employées. L'effet de traitements thermiques simples sur l'évolution microstructurale du matériau extrudé a aussi été caractérisée.

La microstructure a été caractérisée en MET, les textures ont été mesurées par diffraction des rayons X, EBSP en MEB et par mesures d'orientations individuelles en MET. Des essais de traction ont été effectués pour déterminer les propriétés mécaniques. L'analyse de la formation des textures a été complétée par des simulations à l'aide du modèle de Taylor et l'anisotropie des propriétés élastiques a été caractérisée en utilisant les modèles de Reuss, Voigt et Hill.

Une augmentation de la température d'extrusion renforce dans un premier temps la texture de déformation caractérisée essentiellement par une fibre <110> d'orientation parallèle à l'axe d'extrusion. En revanche, à 1250°C, la texture de fibre <110> est partiellement remplacée par une légère fibre <111> associée à l'apparition de la recristallisation. La conservation de la texture de déformation jusqu'à 1200°C est due à la présence de la fine dispersion d'oxyde qui inhibe la recristallisation. Le fait d'introduire 15% de poudre non broyée ne permet pas de modifier les mécanismes d'évolution structurale, et le matériau ainsi extrudé conserve sa texture de fibre <110>.

Les traitements thermiques ont montré qu'au delà d'une température critique, identifiée comme étant la température de transition de phase B<sub>2</sub> ⇒ A<sub>2</sub> (vers 1270°C), une croissance anormale de grains d'orientation <111> intervient sans qu'une recristallisation primaire n'ait eu lieu. En dessous de cette température critique la microstructure est très stable.

**English Version**

B<sub>2</sub> structured Fe 40 %at. Al intermetallics have attracted considerable attention during the last decade. Their elaboration by mechanical alloying, allowing a dispersion of fine reinforcing yttrium oxides, and consecutive extrusion have blast a way to overcome the problems due to their brittleness and poor ductility. The present study deals mainly with the characterization of the influence of some parameters of the elaboration process on the evolution of the microstructures, the textures and the mechanical properties of extruded bars. In order to analyses these evolutions, the extrusion ratio and the extrusion temperature (going from 1000 to 1250°C) were modified. Powders of different natures, containing 15 % of not milled powders, were also used. The effect of simple heat treatments on the microstructural evolution of the extruded material were investigated as well.

The microstructure have been characterized by TEM, the textures have been measured by X ray diffraction, by EBSP using a SEM and by measuring individual orientation in the TEM. Tensile tests were carried out to determine the mechanical properties. The analysis of the formation of the textures have been completed by simulations with the help of the Taylor model and the anisotropy have been characterized by using the models of Reuss, Voigt and Hill.

The increase of the extrusion temperature reinforces in a first time the deformation texture characterized essentially by a <110> fibre texture whose orientation is parallel to the extrusion axis. At 1250°C, the <110> fibre texture is partly replaced by a little <111> fibre related with the activation of recrystallization. The fact that deformation texture is retained up to 1200°C is due to the fine oxide dispersion which inhibits the recrystallization process. The addition of 15 % of atomised powder to the milled powder does not allow to modify the mechanisms of the structural evolution during consolidation. The so-extruded material keeps a <110> fibre texture.

In terms of stiffness, the appearance of the <111> fibre component, for which the Youngs modulus is maximum, is counterbalanced by the important weakening of the <110> component. Therefore this texture evolution has only a very limited influence on the stiffness in the extrusion direction of the bars. The influence of the microstructure of the yield strength could be rationalized by taking in account the hardening due to the grain size, the size of the oxide particles as well as the hardening associated to the presence of matrix defects.



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**Cooperative Research on Related Areas**  
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**France (12/04/2001)**

Le portail Internet "France Contact" a été lancé: ce portail s'adresse aux chercheurs étrangers séjournant ou ayant séjourné en France et permettra le suivi et l'animation du réseau que constituent les milliers de chercheurs étrangers ayant effectué un séjour scientifique au sein des établissements et des organismes de recherche français:

Website : <http://www.francecontact.net>

**Europe (6/03/2001)**

The ESF, on the recommendation of the scientific Standing Committee for Physical and Engineering Sciences (PESC), will support, in fields related to PESC's remit, approximately 10 ESF Exploratory Workshops to be held in 2002.

Each workshop will allow 20-25 leading European scientists to explore novel ideas at the European level with the challenging aim to "spearhead" new and preferably inter-disciplinary areas of research.

In specific terms, PESC's 2001 Call is for workshop proposals on R&D subjects which are NOVEL AND PREFERABLY INTERDISCIPLINARY and which concern emerging fields within any of the following areas: chemistry, physics, mathematics, information sciences, fundamental engineering sciences, materials sciences, and technologies research in these areas.

The PESC Call is available at <http://www.esf.org/physical/WorkshopCalls/Call2001.htm>

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**Job Vacancies, Ph D Position and, Post Doc Position  
Requests – Proposals**

**From Dr. Jack Harrowfield - Australie**

**Job Opportunities**

23/08/2001

[Advanced Nano Technologies Pty Ltd](#)

Nanotechnology.....

Advanced Nano Technologies Pty Ltd is a \$15 million joint venture between Advanced Powder Technology Pty Ltd and Samsung Corning Co Ltd, established to commercialise a patented mechanochemical process used to manufacture NanoPowders.

ANT has recently been awarded a \$2.8 million R&D Start Grant from the Australian Federal Government and as a result, we are currently expanding our Perth-based Research and Development team. Exciting opportunities exist for highly qualified and motivated scientists and engineers to join our R&D team and assist in developing a leading, globally-focused nanotechnology company.

**Positions are available in the following areas:**

Research Opportunities

**Research Scientist -Surfactants/Coatings:** To undertake research and development of dispersants for ANT's nanopowders. You will have a PhD or equivalent experience in surface or colloid chemistry. A good understanding of dispersion science and technology is essential.

**Research Scientist - Particle Coatings :** To undertake research and development of particle surface coatings for ANT's nanopowders to improve chemical stability and facilitate incorporation into various polymers and solvents. You will have a PhD or equivalent experience in surface, colloid and/or polymer chemistry.

**Materials Scientist/Engineer - Nanopowder Synthesis:** To undertake research and development of new nanopowders manufactured by the mechanochemical process technology. You will have a PhD or equivalent experience in Materials Science/Engineering, Solid State materials Chemistry or Solid State Physics.

**Product Engineer - Process Optimisation** : To undertake product development, with particular focus on the optimisation of the manufacturing process for specific nanopowders. You will work with research and production personnel to achieve targeted results. A PhD or equivalent experience in Materials Science/Engineering is required.

Interested applicants should send their CV, with a cover letter explaining how their background and experience will assist them in tackling the challenges of performing research in a newly emerging, rapidly changing industry.

Send To: Human Resources, Advanced Nano Technologies,  
112 Radium St Welshpool, 6106, Western Australia.  
For further information contact Brian: [info@ant-powders.com](mailto:info@ant-powders.com)  
ph (08) 9380 3077, fax (08) 9380 1116  
Closing date: Sep 14th  
[www.ant-powders.com](http://www.ant-powders.com)

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**From Dr. Dr. Deliang Zhang**  
**Ph D Position**

**University of Waikato, New Zealand - 23 / 08/2001**

Titanium PhD Scholarship - Department of Materials and Process Engineering-  
The Department of Materials and Process Engineering at the University of Waikato is seeking a suitable candidate for the Titanium Ph.D Scholarship which has a value of up to NZ\$22,000 per year and is offered for three years. The recipient of the scholarship will be required to conduct research on a suitable topic in the area of processing, characterisation and development of titanium based materials. He/she will work within a dynamic team at Waikato University working on a large research project on processing and development of titanium based materials. The candidate must have a BE (Honours), BSc(Honours), or a Master degree in materials science and engineering or closely related subjects with good average grade

To apply, please send a copy of CV and undergraduate and postgraduate (if applicable) transcript to

Dr. Deliang Zhang, Department of Materials and Process Engineering,  
The University of Waikato, Private Bag 3105, Hamilton, New Zealand,  
Fax: 64-7-838 4835;  
e-mail: [d.zhang@waikato.ac.nz](mailto:d.zhang@waikato.ac.nz).

The application process will remain open until a suitable candidate is identified.

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**From Prof. H.-E. Schaefer**

**Ph D Position**

**Stuttgart - 21/08/2001**

In the framework of the 5th European Research and Development Program The Institut fuer Theoretische und Angewandte Physik, Stuttgart University, Research group of Prof. H.-E. Schaefer has been selected a Marie Curie Training Site and offers a one year position on Nanostructured Materials: Atomic Transport Properties for the Synthesis and Characterization of Novel Soft and Hard Magnets

The Ph.D. student will receive a monthly payment of 1200 Euro plus additional 100 Euro per month travel allowance. Post-Docs should ask us for further details.

Applicants are invited for a 12 month term as a research fellow supported by individual fellowships of the Marie Curie fellowship scheme. The successful candidates will be involved in the synthesis and processing of novel nanostructured materials and composites for soft magnets (Finemet-type) and hard magnets (FeNdB-type), as well as with the investigation of their microstructure, magnetic, and diffusional properties. The gas-phase condensation technique with subsequent compaction under high pressure is used for the production of highly dense nanocrystalline materials. Basic material characterisation will be carried out by x-ray diffraction, differential scanning calorimetry, optical microscopy, and atomic resolution electron microscopy (HRTEM). In addition, several instruments for characterisation of magnetic materials are available. These experimental techniques allow the investigation of a number of phenomena, including: order-disorder transformations, transformation kinetics, phase transitions, and relaxation processes. Furthermore, diffusion studies using the radioactive tracer technique are carried out in order to study the atomic transport properties in nanocrystalline structures.

The candidates have to satisfy the basic criteria of the training scheme as outlined on the Marie Curie Host Fellowship Web site <http://www.cordis.lu/improving/fellowships/home.htm>. As the fellowship forms part of a higher degree project, the candidates should be registered as full-time Ph.D. research students in a well recognized institution. The research interest of the candidates should be in at least one of the following fields: solid state physics, materials science including synthesis and characterization of materials, mechanical and magnetic properties of advanced materials, and structural studies.

The group closely cooperates with the Max-Planck-Institut für Metallforschung, Stuttgart. This collaborative character of the research training provides an additional international profile to the education of the fellows increasing their interaction and eventually their active collaboration with research institutions in different European countries.

Applicants, also Post-Docs, should contact us for further information:

Prof. H.-E. Schaefer  
e-mail <mailto:schaefer@itap.physik.uni-stuttgart.de>  
phone: +49-711-685-5261  
FAX +49-711-685-5271

Dr. W. Sprengel  
e-mail <mailto:sprengel@itap.physik.uni-stuttgart.de>  
phone: +49-711-685-5192  
FAX +49-711-685-5271

<http://www.itap.physik.uni-stuttgart.de/~gsweb/english/index.html>

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#### **Post Doc Position**

##### **Dijon/ France (10/07/2001) – From F. Bernard**

The research group (fine grain materials) from the Research Lab UMR 5613 (Laboratoire de Recherche sur la Réactivité des Solides) is seeking for a post doctoral associate with experience in X – ray Diffraction (experimental and numerical approaches, computer simulation, Monte Carlo ...).

The candidate (he or she) has to demonstrate the ability to work independently, contribute to innovative numerical approach, and develop new projects in this area.

The work will be performed in collaboration between three french labs (Dijon – F. Bernard, Belfort – E. Gaffet, Vitry - Y. Champion).

**Scientific Field :** In spite of a lot a research effort, the mechanism of phase formation during MA is not well understood. It is most often proposed that the process of MA introduces a variety of defects (vacancies, dislocations, grain boundaries, stacking fault,...) which raise the free energy of the system making it possible to produce metastable phases. But there are very few investigations that deal with the characterization and quantification of the defects produced in mechanically alloyed powders. As a primary investigation, the effect of the mechanical activation mode (i.e. the friction or direct shock ones, at least the component ratio of both components) can be assumed on analysing the microstructure of post-mortem milled powders. XRD is really a valuable technique for a characterisation in terms of size and morphology of crystallites and imperfections (microstrains, dislocation, stacking faults,...). Indeed, the ball milling of metals or alloys induces extended variations in the intensity distribution of XRD diagrams and, in particular, in the line profile. Knowledge of the stacking fault density and the twin-fault density is essential to understand the nanomaterials behaviour.

A new line profile analysis method is proposed by Ustinov et al. [123], in order to take into account the dependence of the crystallite size, of the residual strains as well as of the planar defects, on the line profile broadening that may be observed on ball-milled materials. Such a method will allow to understand the influence of ball-milling parameters and for controlling the synthesis of nanostructured materials

**Financial Support :** Regional Financial Support from Burgundy Region in France

Interested candidates should send **correspondence** to:

BERNARD Frédéric - Université de Bourgogne - UFR Sciences et Techniques  
9, Avenue Alain Savary - Laboratoire de Recherches sur la Réactivité des Solides,  
UMR 5613 CNRS / Université de Bourgogne - Equipe "Matériaux à grains Fins"  
B.P. 47870 - 21078 DIJON CEDEX  
fax : 33.3.80.39.61.67 - e-mail : [fbernard@u-bourgogne.fr](mailto:fbernard@u-bourgogne.fr)

*Please note that this proposal is opened for french students.*

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##### **Singapour (11/06/2001) – From Professor L. Lu**

#### **Post-doctoral fellow position**

The position requires candidates with an Ph.D. degree materials science. He/she should have a demonstrated track record on synthesis of metallic amorphous materials. Preference will be given to candidates with relevant experience of mechanical alloying.

The application form can be downloaded from the website:  
<http://www.nus.edu.sg/NUSinfo/Appoint/RESAPPT.HTML>

Please submit your application to  
Associate Professor L. Lu  
Dept. of Mechanical Engineering  
National University of Singapore  
10 Kent Ridge Crescent  
Singapore 119260  
E-mail: <mailto:mpeluli@nus.edu.sg>

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**Brazil (4 / 6 / 2001) – Post Doc Position from Professor Gerardo F. Goya**

The Magnetic Materials Group at São Paulo University is seeking a postdoctoral associate with experience in powder synthesis and magnetism to work on nanostructured ceramics. The candidate should demonstrate the ability to work independently, contribute to innovative experimental design, and develop new projects in this area. Background in at least three of the following areas is desirable: Mechanochemical synthesis. Mechanical alloying. Magnetism in nanostructured systems. Transport measurements. Mossbauer Spectroscopy Scanning/Transmission Electron Microscopy

The candidate should send a curriculum vitae, three representative publications (preferably with the candidate as a first author) and the names, addresses, email and phone numbers of two references that can comment on the candidate's capabilities. Position is open for applicants within three years of receipt of Ph.D. The postdoctoral contract will be one+one year, with salary US\$ ~15000 /y.

Applicants should send the information before 15-August-2001.

Interested candidates should send **correspondence** to:

Professor Gerardo F. Goya  
Laboratório de Materiais Magnéticos  
Instituto de Física - Universidade de Sao Paulo  
CP 66318 Sao Paulo  
05315-970 SP Brazil  
e-mail: [goya@macbeth.if.usp.br](mailto:goya@macbeth.if.usp.br)  
Fax: (55) 11 3818 6984  
Desk: (55) 11 3818 6885

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**France (28/05/2001) – from V. Nivoix**

Proposition de sujet de thèse du

Laboratoire d'Analyse Spectroscopique et de Traitement de Surface des Matériaux,  
UPRES EA 1290, Université de Rouen

**Relation structure-propriétés d'oxydes mixtes nanométriques élaborés par différentes voies de synthèse**

Les ferrites mixtes manganèse-zinc utilisés dans les composants électroniques sont des ferrites doux toujours très utilisés de nos jours, dont les performances peuvent encore être améliorées.

Les propriétés magnétiques, largement conditionnées par la répartition cationique dans les sites de la phase spinelle, dépendent également de la microstructure et plus particulièrement de la porosité et de la taille moyenne des grains dans le matériau final.

Le procédé industriel actuel par voie céramique ne permet pas d'obtenir une microstructure dense à grains fins pourtant très favorable. De nouvelles voies de synthèse sont actuellement explorées, notamment dans le domaine de la "chimie douce".

Nous nous proposons d'élaborer ces oxydes sous forme de poudres nanométriques par broyage à haute énergie et par voie hydrothermale puis de comparer leurs caractéristiques physiques et structurales.

La synthèse par broyage à haute énergie se fera à l'aide d'un broyeur planétaire nouvelle génération (P4 de Fritsch) permettant d'optimiser le broyage par une meilleure maîtrise des paramètres techniques.

Pour mener à bien la caractérisation complète de ces matériaux nous disposerons de différentes techniques telles que la diffraction des rayons X, la spectrométrie IRTF et la spectrométrie Mössbauer pour la caractérisation structurale, la microscopie électronique à balayage haute résolution ou à transmission et la DRX pour la taille et la morphologie, un SQUID pour les propriétés magnétiques. D'autres méthodes d'analyse pourront être mises en œuvre selon les besoins de l'étude. Le candidat ou la candidate devra avoir des connaissances en chimie des solutions aqueuses et sur la caractérisation des matériaux (diffraction des rayons X, spectrométrie IR, spectrométrie Mössbauer, mesure de magnétisme ...)

**Financement** : Nous ferons une demande de financement auprès du ministère de la recherche ou de la région Haute-Normandie.

**Contacts** : Virginie NIVOIX ou Malick JEAN - Université de Rouen - LASTSM-IUT  
76821 Mont Saint Aignan Cedex  
tel 02 35 14 63 59 fax 02 35 14 63 58  
email : malick.jean@univ-rouen.fr

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**SPAIN (03/04/2001)- From J.J. Suñol (joan josep.sunyol@udg.es)**

**Postdoctoral researchers required Universitat de Girona**

Soft magnetic materials obtained by mechanical alloying and rapid solidification: thermal and structural characterization. Analysis of nanocrystallization process.

The research position will involve aspects of: materials processing by mechanical alloying, thermal and structural characterization by DSC, TG, XRD, SEM, TEM, TMS; kinetic modeling.

The position will began with effect from september 2001 to september 2002.

Interested candidates should send correspondence to: Dr. J.J. Suñol.

Department of Physics, EPS (P II). Girona University. E-17071. Girona,

Spain. Fax: 34-972418098.

E-mail: <mailto:joan josep.sunyol@udg.es>

## Bibliographie Récente

### Livres ou "Special Issues"

(21/06/2001)

**From Christian Wohlbier (Scientific. Net Webmaster)**

This is a service of <http://www.scientific.net>

\*\*\* **Materials Science Forum** \*\*\*

Materials Science Forum specializes in the rapid publication of international conference proceedings and stand-alone volumes on topics of current interest. It covers all areas of Materials Science, Solid State Physics and Solid State Chemistry. The periodical is indexed in Science Citation Index and covered by all major abstract media.

Volume 246 until 246 [Surface Coatings for Advanced Materials] and

Volume 207 until 209 [Intergranular and Interphase Boundaries in Materials]

<http://www.scientific.net/msf>

\*\*\* **Solid State Phenomena** \*\*\*

Solid State Phenomena specializes in the rapid publication of international conference proceedings and stand-alone volumes on topics of current interest in the field of solid state physics and its applications to materials science related topics. The periodical is indexed in Science Citation Index and covered by all major abstract media.

Volume 61 until 62 [Contemporary Studies in Condensed Matter Physics],

Volume 59 until 60 [Interfaces and Plasticity] and

Volume 57 until 58 [Gettering and Defect Engineering in Semiconductor Technology]

<http://www.scientific.net/ssp>

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(07/06/2001)

« **Strategic and Technological Watch on Nanomaterials** »

by **E. Gaffet** (1998 – 2000) – 4 CD reports (6.000 analysed references)

Éditeur : Innovation 128 - 24 Rue du Quatre Septembre - 75002 Paris - France - Fax : 33 1 42 65 47 76

Website : <http://www.innovation128.fr/>

(28/05/2001)

**Advanced Ceramic Materials**

\*\*\* **Key Engineering Materials, Volume 122 until 124** \*\*\*

In spite of the very great progress made in ceramic science, and the elegance and excitement of the research which has been

performed, the real driving force for developments in ceramics remains their potential applications. The opportunity for dramatic scientific advances was certainly one reason for the "ceramic fever" of a decade ago, but there is also no doubt that the

prediction of an annual market for fine ceramics, amounting to 6 billion Yen played a role. The challenge is to ensure that ceramics can be successfully introduced into the full breadth of applications where their properties have long made them so appealing. The present volume takes a refreshing and firm step towards the realization of this aim. The publication of a book which sets out to present ceramics from the specific point of view of applications is an event greatly to be welcomed. Systematic organization into various types of application ensures that the reader can fully appreciate the outstanding opportunities offered; and the present limitations. Armed with such a survey, the engineer and scientist will be fully alert to possibilities for progress whenever these arise. 1. Introduction. 2. Electrical and Electronic Functions. 3. Magnetic Functions. 4. Chemical and Physical Functions. 5. Mechanical and Thermal Functions. 6. Biological Functions. 7. Nuclear Applications. 8. Ceramic Coatings. 9. Selected Ceramics with Multi-Applications.

<http://www.scientific.net/kem>

(11/2000) **Information from Fritsch (A. Kohler)**

The subject of the sixth forum part, Fritsch Forum Part VI scheduled for September 14/15th, 2000, will be "high-energy fine grinding". Research and Development demand general-purpose grinding processes which simultaneously exactly define the required energy and the type of stress. This is the only way that reliable results can be achieved when determining activation energies or the mechanical alloying. It must be possible to reproducibly adjust all of the grinding parameters affecting the grinding results.

Participants from research, development and industry will report on demands and novel technological solutions in developing innovative milling technologies. One of the highlights of the event will be FRITTSCH's new Vario-planetary mill "pulverisette 4". This planetary ball mill can simulate ball mills of conventional construction, precisely copy the types of stresses that occur there, and thus reproduce or optimise grinding processes. Due to the great flexibility when selecting the grinding parameters, it is possible to produce results that are unattainable with other ball mills. It is the ideal mill for mechanical activation and alloying. The main applications are in the area of material research and naturally wherever a powerful, innovative laboratory planetary mill is needed.

An extensive report has been written about this event which details and makes readily available the relevant

parts of the lectures and the extensive results of the discussions. Anyone interested can request a copy of the complete report for this forum part VI event on the topic "high-energy fine grinding". Please contact Andrea Köhler, FRITSCH GMBH, Industriestrasse 8, D-55743 Idar-Oberstein, (Phone: 0049/6784/7046, E-Mail: koehler@fritsch.de)

**(7/07/2000) - From Victor Rieckansky Publisher**

Cambridge International Science Publishing <http://www.demon.co.uk/cambsci/homepage.htm>

**MACROMOLECULAR MECHANOCHEMISTRY**

Volume 1: Polymer Mechanochemistry - by Cleopatra Vasiliu OPREA & Florin DAN

Department of Macromolecules, Gh. Asachi, Technical University, 6600 Iasi, Romania

Macromolecular Mechanochemistry presents from theoretical and experimental point of view the main problems of this field, including the results obtained in more than a century of research. It is organised in two volumes: Polymer Mechanochemistry and Polymers with Chemomechanical Functions, respectively. The present volume deals with: Chained Polystage Character of Mechanochemical Process (1), Mechanochemistry of Polymers Deformation (2); Mechanochemistry of Polymer Fracture (including also the Fracture of Composite Materials) (3), and Mechanochemical Processes for Energy Conversion (4). In this frame, the theoretical and experimental material is organised in correlation to the reaction mechanism, the type of mechanical solicitation, and the nature of environmental medium. This book is addressed to professors, students, and researchers involved in the field of polymer science, to engineers from the industry of synthesis and processing of plastic materials, elastomers and fibres, as well as to specialists from all technical domains that exploit polymer-based materials. They will find in the book examination of the theoretical, experimental and applied problems and wide access to the basic literature in this field. Contents

1. Chained polystage mechanism of mechanochemical processes
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4. Mechanochemical Processes for Energy Conversion

Volume 1 (ISBN 189832672X) will be published in September 2000, approx. 500 pages, cased, approximate price £ 80.00; (volume 2 will be published at the end of - 2000)

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**(9/06/2000)**

**"Mechanical Alloying : FABRICATION OF ADVANCED MATERIALS AT ROOM TEMPERATURE"**

**by M. Sherif El-Eskandarany**

(ISBN: 977-299-089-7) Published by DAR AL-FIKR AL-ARABI, Cairo-Egypt.

The price of the book is \$50, and a special discount (20%) is offered to all the RFM member.

Preface

Mechanical alloying (MA) process using ball-milling and/or rod-milling techniques, has received much attention as a powerful tool for fabrication of several advanced materials, including equilibrium, nonequilibrium (e.g., amorphous, quasicrystals, nanocrystalline, etc.), and composite materials. In addition, it has been employed for reducing some metallic oxides by milling the oxide powders with metallic reducing agents at room temperature. The MA is unique process in that a solid state reaction takes place between the fresh powder surfaces of the reactant materials at room temperature. Consequently, it can be used to produce alloys and compounds that are difficult or impossible to be obtained by the conventional melting and casting techniques.

This book intended primarily to serve as an introduction to the MA process, including general description of the process, starting material requirements, the equipment, characterizations of the milled powders, and consolidation techniques, which used to compact the powder into fully-dense bulk materials.

The book contains several typical examples of selected advanced materials that have been fabricated by MA. This book is aimed at either senior undergraduate/post graduate students or materials scientists/metallurgists. - M. Sherif El-Eskandarany - April 2000 - Cairo - Egypt

**(3/02/2000)**

**Two new books on mechanical alloying are now available from Cambridge International Science Publishing (infos fournies par Anne Porter - Publishing Manager - Cambridge International Science Publishing <http://www.demon.co.uk/cambsci/homepage.htm>)**

**1. MECHANICAL ALLOYING - FUNDAMENTALS AND APPLICATIONS**

<http://www.demon.co.uk/cambsci/book52.htm> Contents

Introduction (history, benefits of mechanical alloying); Mechanical alloying (alloying mills, mills in practice, improved mills, the process, parameters);

Variations of mechanical alloying (reaction milling, cryomilling, repeated rolling, double mechanical alloying, repeated forging); Process control agents in mechanical alloying; Mechanical alloying mechanisms (ductile-ductile system, ductile-brittle system, brittle-brittle system, metastable phase formation, amorphisation, nanocrystallization, extension of solid solubility, activation of solid state chemical interaction);

Energy transfer and energy maps;

Consolidation of mechanically alloyed powders (consolidation techniques, thermomechanical treatment);

Mechanical properties of mechanically alloyed materials (tensile properties, fracture, creep, stress corrosion cracking susceptibility);

Modelling mechanical alloying (mechanistic models, deformation, coalescence and fragmentation, evolution of

particle size, milling time, powder heating, powder cooling, atomistic model, thermodynamic and kinetic model) Joining of mechanically alloyed materials; Rapid solidification and mechanical alloying; Applications (nickel-based superalloys, Al-based materials, supersaturated solutions, magnetic materials, mechanically alloyed powders for spray coatings, superplasticity, tribological materials, composites, amorphous solids, nanocrystalline materials, solid-state chemical reactions, etc). ISBN 1898326568, 160 pages 234 156 mm, cased, £45.00, 1999

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**DISPERSION STRENGTHENED ALUMINIUM PREPARED BY MECHANICAL ALLOYING, by M Besterci - <http://www.demon.co.uk/cambsci/book51.htm>**

**1. Characteristics of dispersion-strengthened systems** **2. Mechanical** alloying (kinetics and mechanism of preparation of the Al-C system by mechanical alloying; compaction of powders and heat treatment of compacts; 3. Microstructure and quantitative evaluation of parameters of dispersion-strengthened materials (definition and properties of interparticle distance; experimental possibilities of determination of structural objects; models of heterogeneous structures and their evaluation; simulation of model structures; analysis of the spatial distribution of particles in the Al-Al<sub>4</sub>C<sub>3</sub> material)

4. Static and dynamic mechanical properties (mechanical properties at elevated temperatures; mechanical properties at 20 °C; effect of interface on the mechanical properties; superplastic properties of the system; thermal stability of the system; creep characteristics; creep-fatigue characteristics)

References - ISBN 189832655X, 90 pages, 234 156 mm, soft laminated cover, £25.00, 1999

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**"Mechanical Alloying : Fundamentals and Applications"**

Prof. P.R. Soni, (1999) - Cambridge International Science Publishing

web site : <http://www.demon.co.uk/cambsi/book52.htm>

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**"Nanomatériaux"**

Auteurs : E. Gaffet, S. Begin - Colin, O. Tillement

Editeur : Innovation 128 - 24 Rue du Quatre Septembre - 75002 Paris - France - Fax : 33 1 42 65 47 76

Les dernières années ont vu apparaître dans le monde des matériaux avancés le préfixe "nano" (nanostructuré, nanocristallins, nanophase ou nanométrique) ; les conférences et les forums sur Internet se multiplient où s'échangent des informations sur les avancées scientifiques et technologiques dans ce domaine des matériaux nanostructurés qui se distinguent des matériaux polycristallins conventionnels par la dimension des cristallites les composant ou par la dimension des hétérostructures présentes : ces dimensions sont de quelques dizaines d'angströms, voire de quelques nanomètres. A ces dimensions, les propriétés des matériaux changent radicalement.

Au début des années 90, les japonais ont été les premiers à lancer d'ambitieux programmes de R & D puisque le MITI a consacré aux nanomatériaux près de 200 millions de dollars pour la période 1990 - 2000 et que la Science & Technology Foundation a investi presque la même somme pour co - financer des projets de laboratoires publics et privés. Les Etats Unis puis les pays européens ont investi plus tardivement mais déjà ont obtenu des résultats prometteurs (.....) Certaines applications existent déjà au niveau international, quelque 400 sociétés se partagent aujourd'hui un marché voisin de 1 milliard de dollars mais qui devrait tripler, voire quintupler à l'horizon 2001.(.....)

(...) Pour aider les industriels concernés à imaginer les applications qu'ils pourraient s'approprier et identifier les acteurs internationaux, la présente étude dresse un état de l'art complet des nanomatériaux en décrivant leurs procédés d'élaboration actuels ou envisagés et en détaillant leurs différentes propriétés physico - chimiques et les géométries que l'on peut obtenir.

Enfin l'étude permet de cerner les applications actuelles et potentielles...

**17/09/2001 - From Dr. Eugene Ivanov (TOSOH)  
International Conference  
"Fundamental Bases of Mechanochemical Technologies" •  
Novosibirsk, 2001**

The International Conference Fundamental Bases of Mechanochemical Technologies took place held in the Scientific Centre of the Russian Academy of Sciences situated in Academgorodok of Novosibirsk August 17-21, 2001. This conference was devoted to all aspects of theory, methods and applications of mechanochemistry. The scientific programme consisted of invited lectures, oral, and poster communications. Theoretical aspects of mechanical activation Mechanochemical reactions, kinetics and mechanisms Control of the reactivity of solids by mechanical activation Mechanical alloying Mechanochemistry of organic systems Mechanochemistry for design of new materials including nanosized and composite materials Development of mechanochemical technologies

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**Contributions**

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**High-Efficient mechANOchemical technology of phosphoric fertilizer production by using the nitrous combination**

**J. Amgalan\*, Joe Schon\*\*, A. Minjigmaa\***

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Mechanical processing activates the whole volume of material, not a part. Perennial studies show that mechanical processing is able to change solubility over wide range by adjusting the duration and intensity of processing, as well as by using various additives.

In the literature, there are data depicting the use of organic or inorganic solid, liquid and gaseous combinations.

It is interesting to note that long ago a German researchers (Pat. 101195) offered mechanical way of obtaining phosphoric fertilizers with high content (about 100%, as calculated for P<sub>2</sub>O<sub>5</sub>) of forms soluble in ammonium citrate; however, its introduction has not been carried out yet.

Studies of the activation of Mongolian phosphorites with different nitrogen-containing additives were conducted using the vibrocentrifugal mill (ICCT MAS) and attritors "Union process" (USA).

The present report considers the results of laboratory and semi-industrial tests on the activation of phosphoric and ammoniated phosphate fertilizers, in which soluble phosphate forms (CSP and CASP) are kept at a level about 40%.

As a result of experiments for both the non-continuous and continuous regimes in certain correlations between ore and additives contents, we obtained phosphates present in natural phosphorites, their content being 100 %.

We studied the products of decomposition of phosphate minerals using chemical and physicochemical methods (RPhA, IC-s X-ray and others) and put forward the hypotheses concerning the mechanism of phase conversion of phosphates with the participation of nitrous join under their activation in reactors.

The present technological regulations for the production of activated and ammoniated phosphoric fertilizers by mechanochemical methods are based on large amounts of phosphorites deposited in Mongolia.

### **Chemotoxicological properties of mechanically activated mixture of acidum acetylsalicylicum and lithium carbonate**

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Acidum acetylsalicylicum (AAS) is widely used in medical practice, however, its poor solubility in water superimposes a number of limitations on its application. With the purposes of improving the solubility and the survivability, different components will be used. The selection of lithium carbonate, as the additive to AAS, is explained by its multifactor action on different organs and systems of an organism. For a mechanically treated (MT) mixture of  $\text{Li}_2\text{CO}_3$  and AAS, the solubility was 260 g/l, as contrasted to 2.4 g/l for base mix. According to the data of a Raman Units (RU) method, in the field of 68 and 99  $\text{cm}^{-1}$ , the increase of intensity of absorption bands with time of MT was observed. This is the evidence of intermolecular interactions changing. According to the data of IR-spectroscopy, the intensity of the band with the maximum at 1580  $\text{cm}^{-1}$  (related to C=C oscillations in benzene ring) increases. This is apparently the evidence of a gap in intermolecular connections and the formation of new intramolecular frame. The data of IR and RU-spectroscopies testify that the functional groups do not undergo structural changes, therefore, there is chemical interplay between  $\text{Li}_2\text{CO}_3$  and AAS during MT for 5 hours.

The acute toxicity of a mixture of  $\text{Li}_2\text{CO}_3$  and AAS was investigated on rats. Animals were separated into 6 groups pursuant to the dose of a mixture entering an organism - 1 g/kg, 1,5 g/kg, 2 g/kg, 2,5 g/kg, 3 g/kg, 6 g/kg, correspondingly. As a drug of matching, AAS in similar doses was used. The period of observation was 20 days. The research has shown that the introduction of a mixture of  $\text{Li}_2\text{CO}_3$  and AAS causes the destruction of 20 % of animals that have received a dose of 1,5 g/kg. The percentage of lethality does not change with increasing the dose up to 3 g/kg remaining 20 %. The dose of the mixture of  $\text{Li}_2\text{CO}_3$  and AAS of 6 g/kg produces a 100 % destruction. The analysis of acute toxicity of a broadcast television complex has shown, that 20 % animal perishes only at the introducing of a dose of 2.5 g/kg of weight of a body. The introducing of a mixture  $\text{Li}_2\text{CO}_3$  and AAS is accompanied by an increase of weight of a body animal last day of observation on 55 %, at the introducing of a drug of matching of a AAS - on 54,7 %. In monitoring group the animal increment has compounded 48,6 %.

The organs gorged animal (liver, nephros, heart, intestine) are studied, in which one dilating veins, stasis of a blood in capillary tubes was watched. It is noted, that a mix  $\text{Li}_2\text{CO}_3$  and the AAS in doses up to 3 g/kg invokes a granular and vacuolar dystrophia of an epithelium gyrose canaliculus of nephroses, and at the introducing of a toxic dose (6 g/kg) dystrophia of change reached a necrobiosis and necrosis. Simultaneously with these, rough damages of hepatic cells take place. In the survived animals, the dose  $\text{Li}_2\text{CO}_3$  and AAS up to 3 g/kg invoked a small focal edema of a mucosa of a colon, in too time in monitoring group in this dose the drug promoted development of an even edema slimy both submucosa thick (heavy-gauge) and caudal department of a small bowel from moderate up to expressed.

The pathological operating of a toxiferous mix expressed basically in development of changes in the myocardium, liver, nephroses, in subtoxiferous - changes in an intestine.

Preparation of dispersed ceramic materials by soft mechanochemical synthesis

**E.G. Avvakumov, L.G. Karakchiev, A.A. Gusev, O.B. Vinokurova**

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Specific features and outlooks of soft mechanochemical synthesis as a method to obtain dispersed ceramic materials are considered. The problems connected with the formation of new phases and dispersed particles during mechanochemical activation followed by thermal treatment are discussed. The advantages of soft mechanochemical synthesis are demonstrated for the synthesis of  $\text{ZrTiO}_4$ ,  $\text{Al}_2\text{TiO}_5$ ,  $\text{ZrSiO}_4$ ,  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$  and other complex oxides.

It is known that the dispersed state and morphology of the final products of thermal synthesis are determined by the mechanisms of formation and growth of the nuclei of the crystal phase of the product. Mechanical activation of mixtures can serve as a method to generate the nuclei, since local high temperature and pressure are formed during activation, thus providing the conditions under which micronuclei of the new phases appear at the contacts between the reacting particles.

The formation of dispersed particles during mechanical activation of the mixtures of hydrated titanium dioxide and zirconium dioxide was investigated and compared with mechanochemical reactions of anhydrous oxides. The changes of dispersed state and crystallite size during thermal treatment has been followed within a wide temperature range. Hydrated zirconium titanate is likely to be formed when the soft procedure is used; only one product  $ZrTiO_4$  is crystallized from it at  $600^\circ\text{N}$ . Mechanical activation of a mixture of anhydrous oxides gives crystal  $ZrTiO_4$ , its amount being 35%; it increases slightly when heated to  $800^\circ\text{N}$ .

The formation of hydrated aluminium titanate is observed in the activation of a mixture of hydrated aluminium and titanium oxides. However, at temperatures above  $600^\circ\text{N}$  it decomposes to give aluminium and titanium oxides; then, only at temperatures above  $1300^\circ\text{N}$  crystalline aluminium titanate is formed.

In the investigation of the synthesis of zircon by thermal treatment of mechanically activated mixtures of zirconium and silicon oxides, the existence of an optimal water content providing the maximum efficiency of the synthesis was discovered.

It was stated in the synthesis of cordierite from natural hydrated oxides (talc, kaolinite, gibbsite) that spinel  $MgAl_2O_4$  is not formed during the thermal treatment of mechanically activated mixtures, (while it is formed in the mixtures of anhydrous oxides), that simplifies the synthesis and allows to decrease the temperature at which the initial product is formed to  $1260^\circ\text{N}$ .

The application of soft mechanochemistry allows substantial improvement of classical technological schemes of the synthesis of ceramic materials.

### **Molecular dynamic modeling of the (100)-(111) boundary in the Lennard-Jones crystal**

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The structural and transport properties of the (100)-(111) boundary in the Lennard-Jones crystal was studied by molecular dynamic technique. The problem of boundary properties arises from experimental investigation of changes in bulk properties of substance during the nanocomposite formation. In the case of nanocomposites formed from chemically inert aluminium oxide and ionic salt with ionic conductivity, the decrease of the superionic transition temperature was observed. It is shown in our work that at temperature about 0.75 of the system's melting point, fast atomic motion along the boundary starts. Analysis of the model structure by Voronoi-Delone tessellation method showed no qualitative changes at this temperature. In the model system, recrystallisation processes and motion of the boundary are not observed, all atomic motions are localized in the boundary region. Because of the absence of changes in the boundary structure, we suppose that no phase transitions occur at the temperature at which fast motion begins. The fast motion could be explained in terms of lowering of diffusion activation energy near the boundary with high density of defects.

The research described in this publication was made possible in part by Award No. REC-008 of the U.S. Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CRDF) and was supported by the Russian Foundation for Basic Research (project N 00-03-32523).

### **The mechanochemical synthesis of materials based on iron silicide**

**E.Yu. Belyaev, G.A. Suchkova, O.I. Lomovsky**

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Iron disilicide is the cheapest and ecologically friendly thermoelectric material. Mechanical alloying is the best method to synthesize iron disilicide. The elements such as cobalt, aluminum, manganese, boron, chromium and others, used to dope iron disilicide, affect the mechanochemical interaction of silicon and iron. Because of strong dependence of thermoelectric efficiency on doping level, it is important to understand how the doping elements get input into iron disilicide during mechanochemical synthesis. The goal of our work was to investigate the process of mechanical alloying of iron disilicide. The synthesis was carried out in high-energy planetary ball mills AGO-2 and APF-4. The intensity factor was varied by using the balls with different diameter (3-15 mm) at fixed (600 m/sec<sup>2</sup>) acceleration. The synthesized samples were analyzed by the X-ray diffractometry on synchrotron radiation beam and by the method of differential dissolution.

At the initial period of mechanical treatment, the formation of a solid solution of silicon in iron took place. The dependence of the amount of solid solution on treatment intensity was investigated using undoped samples. Chromium and boron were used as simulative dopants. They have different solubility in the components of mixture. We suppose that there are two different ways of impurity injection during mechanical treatment:

- 1)  $Fe+2Si+D \rightarrow Fe(Si,D)+Si \rightarrow FeSi(D)+Si_{am} \rightarrow FeSi_2(D)$ , in case of iron-soluble dopant (Cr)
- 2)  $Fe+2Si+D \rightarrow Fe(Si)+Si(D) \rightarrow FeSi+Si_{am}(D) \rightarrow FeSi_2(D)$ , in case of silicon-soluble dopant (B)

It was shown that boron content does not affect the lattice parameter of products but affects the rate the formation of an intermediate compound FeSi. Chromium affects lattice parameters of both iron and iron monosilicide. Chromium concentration has no effect on the rate of mechanochemical interaction. Thus, using the dopant solubility in the intermediate or amorphous products we can control the mechanisms of its intake during mechanochemical synthesis.

The research described in this publication was made possible in part by Award No. REC-008 of the CRDF (USA).

### **The mechanochemical synthesis and compacting of thermoelectric composite materials based on beta-FeSi<sub>2</sub>**

**E.Yu. Belyaev, G.A. Suchkova, A.I. Ancharov, G.V. Golubkova, S.S. Avramchuk, O.I. Lomovsky, V.I. Maly\*, A.A. Vlasov\*\*, L.S. Dovlitova\*\***

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The iron disilicide is a good candidate for the mass production of thermoelectric generators for civilian application. Efficiency of doped FeSi<sub>2</sub> leaves much to be improved. Ceramics thermoelectric properties were formed basically at the stages of doped iron disilicide synthesis, sintering and annealing. There are many ways to improve the efficiency of FeSi<sub>2</sub> based materials: 1) the particle size decreasing; 2) the synthesis of FeSi<sub>2</sub>-metal oxide composite materials; 3) the superlattice (nanocomposite FeSi<sub>2</sub>-semiconductor, such as SiC) preparing from iron disilicide; 4) nonconventional and multicomponent doping of iron disilicide Fe<sub>1</sub>-XD<sub>X</sub>Si<sub>2</sub>-YDY.

The purpose of this work was to synthesize composite material and ceramics based on doped iron silicide. Starting from elements, the iron disilicide powders were prepared by the method of mechanical alloying in the high-energy planetary ball mills AGO-2 and APF-4 type, ball acceleration 600 m/sec<sup>2</sup>. The ceramics sintering was carried out in vacuum 10<sup>-5</sup> torr or pure argon atmosphere in conventional heater. The blast wave compacting was carried out under different detonation velocity of explosive. Ceramics was analysed by conventional X-Ray analysis (DRON-3, CuK $\alpha$ ) and by means of synchrotron radiation diffraction on VEPP-3, INP SB RAS. The phase content of samples under mechanical alloying and explosive compacting was analysed by differential dissolution method. Thermoelectromotive force of ceramics was measured within the temperature range from room temperature to 5000C. Particle sizes of powder materials and grain size of ceramics were analysed by electron and optical microscopy.

The composite material was formed from initial mixtures of components by different mechanisms depending on composition and treatment condition. In case of excess of dopant elements in FeSi<sub>2</sub>-XD<sub>X</sub> we observed FeSi<sub>2</sub>-FeSi or FeSi<sub>2</sub>-dopants phase composite. This composite type improved thermoelectric properties increasing  $\sigma$  due to the metallic character of conductivity of FeSi and other silicides.

The composite FeSi<sub>2</sub>-SiO<sub>2</sub> materials were formed under mechanical treatment of initial mixtures of iron disilicide and SiO<sub>2</sub> powders. In case of chemical reaction of silicon and iron under mechanical treatment in air in jars, the composite FeSi<sub>2</sub>-SiO<sub>2</sub>-FeSi was formed.

The differences in morphology, phase content and the distribution of doping elements between phases of ceramics were demonstrated using the samples compacted with different explosive intensity. But electrical measurements demonstrate that there are no direct inter-relations between explosive intensity and thermoelectromotive forces.

The combination of mechanochemical synthesis of FeSi<sub>2</sub>-based composite powders and explosive compacting method produces the thermoelectric ceramics with nano scale grains size and nonequilibrium phase content. Under working temperature up to 4500C this ceramics can be used without grain size growth process and demonstrate good thermoelectric properties.

The research was supported in part by Award No. REC-008 of the CRDF (USA).

About the history of mechanochemistry in Siberia

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1. The first mechanochemical studies in Russia. Investigations carried out by Flavitsky, Kholevo, Andreev, Isakov, Voskresensky during pre-war and post-war periods.

2. Pre-conditions for the first mechanochemical investigations in Siberia. The scientific school of the Solid State Physics in Tomsk (Kuznetsov, Tartakovsky, Vorobjev, Presnov, et al.) and its influence on research in Chemistry (Buntin).

3. The post-war trend to carry out investigations aimed at the assistance in reconstructing the national economy. Investigations dealing with the application of the method of qualitative analysis of ores under field conditions in Siberia (Boldyrev, Sakovich, Yakovlev).

Attempts of the first works in the theory of mechanochemical synthesis: where does the interaction take place – in liquid or in solid phase?

4. Organization of the Siberian Branch of the Academy of Sciences of USSR. Investigations carried out at the Institute of Geology and Geophysics AS USSR on fine and ultrafine grinding of ores. Comminuting extractor by Golosov. Investigations of Molchanov, Gusev, Yusupov into intensification of enrichment and treatment of mineral raw materials.

Works of Boldyrev and Avvakumov in the Institute of Chemical Kinetics and Combustion SB AS USSR, and Logvinenko and Savinkina at the Institute of Mineral Raw Processing SB AS USSR on the intensification of recycling of ores and the technologies for the preparation of materials for new technics. Development of new types of mechanical activators, including flow-through ones.

Investigations into the theory of mechanochemical processes. Verification of the thermal theory. What happens at the nose of a crack? A kinetic model (Boldyrev, 1972), the hypothesis concerning hydrothermal processes in mechanochemical activators.

Investigations in the area of mechanics of processes that occur in mechanochemical activator (Zhyrnov).

5. The Laboratory of Kinetics of Chemical Reactions in Solid Phase goes over to the Institute of Physicochemical Foundations of Mineral Raw Processing. Mechanochemistry as a direction to become the single profile of the Institute. Main goals: intensification of technological processes in construction industry, mineral raw processing at the stage of primary treatment, including rare metals, acid-free methods of processing phosphorus-containing ores into mineral fertilizers. Lithium technology. The first results on mechanical alloying (Pavlyukhin, Avvakumov, 1975).

Theoretical studies: mechanochemistry of ferrites (Pavlyukhin), pulsed character of mechanical action (with respect to time and space).

6. Attempts to unite the efforts of scientists working in the area of mechanochemistry in the Siberian Branch. The development of the general research Program. Development of large-scale semi-industrial mechanical activators. Organization of the All-Union Meetings on the Mechanochemistry of Inorganic Substances. Strengthening of international linkage. Establishment of contacts with the German and Slovak teams of mechanochemists. Participation of Siberian scientists in TATARAMAN, in conferences on mechanochemistry and mechanoemission in DDR. Start of Soviet-Japanese contacts in mechanochemistry.

Organization of the Scientific and Technical Commission on mechanochemical devices for mechanochemical activation at the State Committee on Science and Technology. Creation of the International Mechanochemical Association at the IUPAC. Soviet-Japanese symposia on mechanochemistry. INCOME as an international mechanochemical forum. Participation of mechanochemists in Scientific and Technological Commission of Experts. Organization of bibliographic bulletin on mechanochemistry.

Scientific results of this period. Development of mechanochemical synthesis. Mechanochemistry of intercalation into gibbsite (Berger, Boldyrev, Kotsupalo). Development of structural investigations of oxide systems. Development of investigations of mechanically activated phosphorus-containing ores (Chaikina, Kolosov, Boldyrev). Start of investigations into mechanical alloying. Preparation of icosahedra. Hydrogen energetics (Ivanov, Stepanov, Konstanchuk, Bokhonov). The first monographs on mechanochemistry (Molchanov, Avvakumov, Boldyrev). Calculations of temperature and pressure peaks in mechanical activators (Urakaev). Soft mechanochemical synthesis (Avvakumov). Mechanism of the mechanochemistry of the halides of alkaline metals (Goldberg, Pavlov).

7. Post-perestroika period. Decrease of the financial support from the State, self-supporting agreements. Decrease in international communications. Search for new application areas. Synthesis of hydrogenation catalysts (Ivanov, Fasman). General principles of the application of mechanochemistry in catalysis (Buyanov, Molchanov). The synthesis of new catalysts for oxidation – reduction (Sadykov), investigations in the mechanochemistry of ore concentration processes (Yusupov). Application of soft mechanochemical synthesis for the creation of new materials (Avvakumov).

Application of mechanochemistry to small-scale organic synthesis and pharmacy (Boldyrev, Dushkin, Shakhtshneider). Application of mechanochemistry in the synthesis of functional ceramics and processing of the natural organic raw materials (Lomovsky). The role of liquid phase in mechanochemical processes (Gerasimov). Mechanochemical cosmetics (Boldyrev, Grigorieva). Design and production of industrial mechanochemical activators (Denisov).

8. Present time. Attempts to come to the question which had been asked at the very beginning: what happens in a solid when it is loaded hydrostatically (Boldyreva) and by shift (Politov). Start of systematic investigations into the behaviour of molecular crystals under mechanical loading (Boldyreva, Shakhtshneider, Politov, Boldyrev). Calculations of the relations between heat released in course of reaction and the Joule heat (Urakaev). Attempts of practical application of soft mechanochemistry in industry (Avvakumov). Creation of the technology of aspinat – one of the first medical preparations in the world

obtained by means of mechanochemistry. Computer simulations of processes occurring in ionic crystals under mechanical loading (Pavlyukhin, Gainutdinov).

9. Attempt to look into future.

### **Thermal stability of nanostructure in rapidly solidified Al-2% Zr alloys after severe plastic deformation**

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Detailed investigation of the ultrafine structure of rapidly solidified Al-2% wt. Zr alloy after severe plastic deformation (SPD) has been carried out. The transmission diffraction electron microscopy and the method of the X-ray structural analysis were used for structure evaluation.

Rapidly solidified disk billets ( $\varnothing$  80x0,6 mm) of the Al-2% Zr alloy were produced using the equipment for centrifugal casting (the cooling rate was  $2 \times 10^4$  K/s). SPD processing of cast billets, 10 mm in diameter, was performed by high pressure torsion (HPT) using the strain rate of 1 turn/min and pressure of 5 GPa at room temperature. The number of turns was equal to 5. These deformation conditions provided true strain of the material about 5. The annealing of deformed material was carried out at temperature from 373 to 773 K.

Prior to SPD processing the samples had two-phase structure containing grains of plastic Al matrix and brittle Al<sub>3</sub>Zr metastable intermetallics with cubic lattice.

It was established that the combined treatment of the Al-2% Zr alloy in liquid and solid state (a rapid solidification from a melt and SPD by HPT) resulted to ultrafine grained structure with grain of 300 nm in size and high microhardness  $H_v = 1200$  MPa. The total supersaturation of the Zr in the  $\alpha$ -phase attained after rapid solidification and subsequent HPT deformation processing.

Special attention was given to the changes in the microhardness and in the grain size during different heatings of deformed material. The results of microhardness tests, TEM and X-ray methods showed a consequent of an evolution of processes during the heatings, such as stress relieving, an artificial ageing and a recrystallization. The relation between a micro structures and mechanical properties during annealings was also obtained.

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### **The Problems of Quantitative Description of Mechanochemical Processes**

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In mechanochemical processes of a  $A_{sol} + B_{sol} = AB_{sol}$  type, mechanical treatment of the reaction mixture results in the creation of a composite, consisting of the initial reagents with the sizes of crystalline blocks varied from several to tens and hundreds of nanometers and with the area of interface up to tens of  $m^2/g$ . Interpenetration of the atoms, which precedes the formation of the products in such systems, either are caused by the action of mechanical forces or are carried out by diffusion mechanism. The differences between the mechanisms of atom migration are not distinctive and can be identified. In a number of cases, both mechanisms occur simultaneously.

The difficulties appear as soon as the necessity arises to describe quantitatively the dynamics of mechanochemical transformations. In the current report it was shown that under particular conditions, the dynamics of consumption of the parent reagents and (or) the formation of the products are unambiguously determined by the amount of energy introduced in the system. This fact made it possible to use physically valid parameters, which can be measured experimentally, for description of these processes. For instance, the stages of interface formation and interpenetration of atoms are characterized by the value of the specific energy consumption.

In the current report, the results of the quantitative description of the processes of mechanical activation, the reactions of solids with gases, and the synthesis reactions in the mixtures of reagents were considered. In addition, the relation of the values of the chosen parameters and the reagent properties and conditions of mechanical treatment are discussed on the basis of particular examples.

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### **MECHANO-CHEMICAL SYNTHESIS OF FLUOROAROMATIC COMPOUNDS**

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One of the ways to synthesize fluoroaromatic compounds is to carry out the substitution of chlorine atom with fluorine using metal fluorides as a source of fluorine. In industry, the fluorination of chloroaromatic compounds is carried out either in an autoclave at high pressure without solvent, or in aprotic solvents at atmospheric pressure. The described ways of synthesis are characterized by high temperatures and duration of reaction, as well as the significant amount of wastes formed. The goal of our investigation is the synthesis of fluoroaromatic compounds using mechanical activation permitting considerable acceleration of solid-phase chemical process [1].

The experiments were conducted by joint treatment of a mixture of reagents in a planetary - centrifugal grinding mill. Alkaline and earth metal fluorides and their mixtures were used as the fluorinating agents. Naphthalene octachloride, pentachloropyridine and hexachlorobenzene were taken as the predecessors. The influence of the nature and excess of the fluorinating agent, and also the duration of joint treatment on fluorination process was studied. It was shown that the depth of reaction of fluorination in each particular case was determined by experimental conditions and the nature of reagents.

As a result of the conducted investigation, the principal possibility to carry out the reaction under the conditions of mechanical treatment of a mixture of initial reagents is shown. The developed mechanochemical way of carrying out the reactions of fluorination of chloroaromatic compounds can be used for other processes of organic synthesis.

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## **MECHANOCHEMISTRY OF NATURAL AND SYNTHETIC APATITES AND ORTHOPHOSPHATES IN MULTICOMPONENT SYSTEMS AND ITS TECHNOLOGICAL PROBLEMS**

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Mechanical activation and mechanochemical synthesis of apatite are two opposite processes. The mechanical activation of natural apatites and phosphorites is one of the promising ways to obtain phosphate fertilisers. Phosphate ores are multicomponent systems (apatite, calcite, dolomite, quartz, and other) with fine penetration of minerals. It has been revealed that the relative stability of minerals with respect to mechanical action depends on their hardness, composition and structure of minerals and ore in general, increasing in row: layered silicates and aluminosilicates < carbonate minerals < apatites < quartz. Mechanical stress that exceeds the dynamic yield strength in the solid is the necessary condition [1]. In order to achieve apatite activation in presence of other minerals in phosphate ores, a mechanical action is needed so that value of dynamic yield strength for the ore in general exceeded its minimal value for apatite. The dynamic yield strength for apatite determined from sclerometric measurement of microhardness was found to vary within the range 1 - 2,7 GPa. The dynamic yield strength of phosphorites depend on elastic constants of minerals that form ores. An average value of the dynamic yield strength was 1 GPa for carbonate phosphorites, 1,44 GPa -for siliceous-clay and 2,04 GPa - for siliceous phosphorites. It has been revealed that the decrease of hardness and the elevation of plasticity phosphorites demands mainly attrition regime of activation. Optimal parameters of mechanical activation have been determined for the phosphate ores of different mineral composition - it is impact-attrition regime at the stress of 1-4 GPa. The activators of continuous operation with low energy consumption have been designed, their productive capacity being 1 and 3 t/h. The technology has been realised at the small-scale industrial works on the basis of the Burenkhan deposit in Mongolia [2].

The possibility of directed mechanochemical synthesis of the compounds of complicated composition and structure by means of mechanical activation of multicomponent mixtures has been demonstrated for orthophosphates and isomorphous modifications of apatite as an example. The influence of relations between the structures of the initial substances and final product on the kinetics and mechanism of mechanochemical synthesis is shown. Chemical transformations between the components in the activated mixture are demonstrated to go on during the storage at room temperature. The character of the processes that occur during mechanochemical synthesis of various apatites has been discovered to be reversible. The stages interaction of components in system  $Ba(H_2PO_4)_2$  -BaO - BaF<sub>2</sub> - Cu<sub>2</sub>Met. and in the parts of it (two- and three- component ) by electron microscopy, IR, X-ray have been studied. Kinetic energy diagrams show that depending on the amount of the energy supplied to the activation zone the composition of the formed phases is changed and the mechanochemical synthesis can be ceased at a required stage of the process. Mechanochemical method allows to synthesise the compounds with complex structures of the given composition in multicomponent system [3].

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2. V.V. Boldyrev, et al, Ibid, p. 95-98.
3. M.V. Chaikina, Ibid, v. 6, 1998, p.135- 144.

## **MECHANOCHEMICAL TECHNOLOGY OF PRODUCING PHOSPHORUS-CONTAINING FERTILIZERS**

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An ecologically safe mechanochemical technology of producing phosphorus-containing and complex fertilizers from phosphate ores of different genesis and mineral composition has been developed [1]. Mechanical activation of phosphate ores in special mills results not only in their dispersion but in the transformation the apatite into the amorphous phase and partially into  $\beta$ - and  $\alpha$ -tricalcium phosphate:  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \rightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaF}_2$ ; in consequence - transformation of the phosphate to dissoluble in wet soil condition form. This phosphate is able to be assimilated by plants.

More than 30 phosphate ore deposits have been investigated in Russia, the FSU countries, Mongolia. Optimal parameters of mechanical activation have been determined for the phosphate ores of different mineral composition. The activators of continuous operation with low energy consumption have been designed in ISSC SB RAS, their productive capacity being 1 and 3 t/h. [2].

Flow sheet of production of phosphoric fertilizers by mechanochemical method:

**CRUSHING  $\Rightarrow$  MECHANICAL ACTIVATION**

Long-term agrochemical tests (for 15 years) of mechanically activated ores of different composition have been carried out by the Siberian Institute of Agriculture and Chemization and a series of the institutes and agrochemical establishments of the Krasnoyarsk district and Far East at wide range of soils and with various crops. These tests demonstrated high fertilizing effect which was not less than that of triple superphosphate.

The technology has been realized at the small-scale industrial works on the basis of the Burenkhan deposit in Mongolia [3]. The ISSC has produced and sold in 1997-2000 an experimental series of mechanically activated phosphate ores for use at the personal plots and farms.

*The advantages of the developed technology compared to the traditional methods of producing phosphorus fertilizers are:*

- ◆ small investments into the construction of works;
- ◆ the use of ores which are substandard for the known technologies;
- ◆ the possibility of developing the deposits with small ore resources;
- ◆ simplicity of the technological line including grinding and activation;
- ◆ ecological safety of the technology.

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***Autowave propagation of solid state reaction front due to positive feed-back between reaction and stress relaxation by fracture  
(By the example of ionic exchange in lime silica glass)***

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The kinetics and spatial development features of  $\text{Na}^+$  to  $\text{Li}^+$  ionic exchange in soda lime silica glass taking place in lithium containing melts have been studied. Reactions of this type are known to proceed by means an ionic interdiffusion mechanism. But the reaction under consideration has a specific feature. At the ionic exchange under the temperature lower than that of glass transition, the volume misfit due to this reaction induces stress generation in glass, which leads to the product fracturing. The fracture removes diffusion difficulties of the ionic exchange and so promotes acceleration of the reaction. The positive feed-back between the reaction and the fracture defines reaction front velocity, morphology of fracture and characteristic size of the fractured product's fragments. This reaction can be considered as a modelling solid state reaction of thermal decomposition type. Therefore, creation of the mathematical model of its macrokinetics would be very useful for solid state chemistry.

The appearances of spatial and temporal self-organising in the investigated reaction have been found out. Depending on the melt composition, completely differing solid product morphology types are observed at the same reaction: systems of ranked hexagon rods (in chloride melts), crimped rods (in a mixture chloride - nitrate) and disorderly system of plates (in nitrate melts). It is shown, that the occurrence of spatially ranked system of rods at ionic exchange is caused by a solidification of the exchange product melt near to the crack's tips at the fracture front.

Two kinetic models of reaction/fracture front have been created, one for plate-like disorderly fracture morphology and another for ranked morphology of rods. The results of numerical computations performed on the basis of these models allow to predict such characteristics of the reaction/fracture front as the rate and specific fracture scale as well as stability of the reaction front of certain morphology.

The experimental results are well described by the model constructed on the basis of the feedback concept.

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***influence of grinding on the texture, structure and thermal stability of siderite, dolomite and ankerite***

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The influence of grinding on the textural and structural properties of magnesium substituted siderite and double magnesium and calcium carbonates has been studied. The crystal size,  $D$ , and the level of microstrains,  $\epsilon/2$ , has been measured from the broadening of the X-ray profiles. It was found that a continuous decrease of the crystal size and an increase of the microstrains as a function of the grinding time takes place until reaching a steady state after 1 or 2 hours of grinding and then  $D$  and  $\epsilon/2$  remains constant if the grinding continues in progress. The inverse relationships found between the crystallite size and the level of microstrains has been explained by assuming that the particles are constituted by a number of crystallites welded in a mosaic structure and that the grain boundaries constitute the main contribution to the microstrains. The comparison of the particle sizes determined for the as received and ground samples from BET specific surface measurements with the corresponding crystallite sizes determined from the broadening of the XRD peaks supports this assumption. XRD analysis pointed out of the whole set of ground minerals that phases different from those existing in the starting minerals were not observed. TG, DTG and XPS analyses showed that the grinding of calcium and iron carbonates partially substituted with magnesium leads to a segregation of  $Mg^{++}$ . Thus, the thermal decomposition under vacuum of the unground ankerite and dolomite samples takes place in a single steep that mainly leads to the formation of  $MgO$  and  $CaO$ , while the final product of the thermal decomposition of magnesium substituted siderite is a magnesium-iron oxide solid solution ( $Fe_xMg_{1-x}O$ ). However, the decomposition of the ground samples take place in two steeps, the first one corresponding to the  $CO_2$  weight loss associated to  $Mg^{++}$  and the second one associated to the thermal decomposition of either calcium carbonate or iron carbonate. The percentage of contribution of the first steep with regards to the second one increase by increasing the grinding time. Moreover, periclase ( $MgO$ ) and magnetite ( $Fe_3O_4$ ) are the final products of the thermal decomposition of the ground siderite under high vacuum. An explanation of this behaviour is given.

#### **SOLID STATE REACTIONS IN THE Fe-C SYSTEM UNDER MECHANICAL ALLOYING**

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The sequence of structure-phase transformations under mechanical alloying powder mixtures of Fe and C in the atomic ratios Fe(75)/C(25) and Fe(68)/C(32) has been studied by X-ray diffraction, Mössbauer spectroscopy and magnetic measurements.

The initial stage of mechanical alloying (MA) is characterized by a sharp decrease of the  $\alpha$ -Fe grain size down to 4 nm, penetration of C along the grain boundaries and formation of an amorphous Fe-C phase in the interface region (boundary and close-to-boundary distorted zones). The C concentration in it is equal about to 25%. The maximum amount of the amorphous phase does not exceed 40%.

Increasing grinding time results in decreasing the fraction of the amorphous phase and in forming a distorted  $Fe_3C$  carbide (cementite). On grinding the 75/25 mixture almost 100% cementite is obtained at the final stage of MA. In the case of the 68/32 mixture the maximum amount of cementite is equal about to 50%. With increasing grinding time a transition from cementite to a high C concentration non-equilibrium  $Fe_7C_3$  carbide with an orthorhombic structure takes place. It is a dominating phase (~ 90%) at the final stage.

Microscopic mechanisms of mechanical alloying are presented in the report.

The work has been supported by the Russian Foundation for Basic Research (project No. 00-03-32555).

#### **MECHANOCHEMICAL ORGANIC SYNTHESIS and PREPARATION of NEW MATERIALS**

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Application of solid state mechanochemical processes in laboratory practice and in chemical technology, from our point of view, may have a number of advantages connected to refusal of use of solvents, reduction of common time of realization of a process, and also opportunities of preparation of new unusual products. In the report, four variants of products of mechanical activation of mixtures of solid substances are considered:

1. Preparation of "reactive" materials (aggregates of particles).
2. Preparation of "solid solutions" of chemically not interacting components.

3. Preparation of organic compounds by interaction between solid reagents.
4. Preparation of crystal phases with high concentration of defects and increasing their reactivity in the subsequent chemical reactions.

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**Rotor turbulent oval-maker  
as a device to correct the shape of particles**

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Along with other physicochemical characteristics, the shape of particles comprising the powder material is often substantially important for the quality and properties of the products made of these materials. We developed a new type of device that allows us to obtain oval isometric particles with a size of 20 micrometers to 2-3 mm from a material of any hardness including diamonds. The operation of the rotor turbulent oval-maker is based on the generation of turbulent gas flows under which the particles collide with each other thus treating the surface of each other. If a particle has got any defect, for example a latent crack, it gets cleaved along the defect site and the parts go on being treated. So, the material with increased strength characteristics of the particles themselves is obtained, which is important, for example, for abrasive powders. The outer layer (1-2 micrometers thick) of particles turns out to be highly defective when treated in the device, which is likely, for example, to intensify agglomeration processes during subsequent use of the processed powders.

The use of iron and steel powders as a raw material for the preparation of construction details by means of powder metallurgy requires metal powders with specific properties. One of important factors is the consistency of powder, as well as the bulk density in case when the powder is filling the void of a matrix. These factors finally have an effect of density which can be obtained, and hence an effect on the quality of the product after agglomeration. All the above-mentioned properties are mainly connected with the grain shape and the granulometry of the powder used in the process. It is clear that the closer is the shape of a separate grain to the sphere, the higher are consistency and bulk density.

The treatment in oval-maker allows us to obtain metal powders composed practically completely of oval grains that are nearly spherical. The experiments on the treatment of the stainless steel (PROH18I10) powders and titanium (PTM) showed the efficiency of oval-making. Bulk density of the powders increased after treatment by a factor of 1.3-1.5 and reached 75-85% of the theoretically possible figure.

**NEW COMPOSITE MATERIALS PRODUCED BY THE METHOD OF  
MECHANICAL ALLOYING**

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The method of mechanical alloying has been used to produce new powdered, aluminum-based materials. As alloying constituents magnesium, copper, titanium, scandium, lanthanoids, boron, silicium, silicium carbide and lanthanoid oxides were used.

The composites containing 10 weight % boron and titanium each, as well as those containing 10 weight % boron and silicium each, and 20 weight % scandium can be used by pertinent industries as master alloys.

The composite on the basis of aluminum with 25 weight % SiC and Cu (3.2. weight %), Mg (1.2 weight %), having high values of ultimate strength and hardness, may find an application in the production of lighter-than-conventional structural materials in machine- building.

Powdered materials on the basis of aluminum containing up to 20 weight % boron or lanthanoids and their oxides, as well as various combinations of boron and lanthanoid mixtures (or their oxides) may be used as structural or engineering materials when creating and operating transport containers for storage of spent fuel. These materials have serious advantages over the conventionally employed boron steels. They are lighter, have comparatively higher (up to 20%) contents of the component with a high value of effective neutron-capture cross-section. Their high thermal conductivity may be important for prolonged storage of spent fuel, since it prevents the container from being overheated. Moreover, by proper selection of the combination of alloying constituents it is possible to adapt the material for use as a neutron detector in a certain region of the

distribution of power. By employing traditional technologies (extrusion, hot pressing, etc.) these materials can be used to make constructional elements such as sheets, channels, angle pieces, etc.

Researches of corrosion behavior of materials on the basis of aluminum alloyed with boron or lanthanoids (or structures with their simultaneously presence) now are begun in modeling environments characteristic for conditions near on parameters to an emergency condition of containers, containing the defective fuel elements with high burning out of nuclear fuel.

The patent of Russia <sup>1</sup>. 2113941 protects the submitted developments.

### computer simulation of intensive mechanical action on solids

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The 2D Lennard-Jones, complex ionic AB<sub>2</sub>O<sub>3</sub> and 3D Lennard-Jones systems were investigated by the molecular dynamic method to study the structure changing mechanisms in the solid under intensive mechanical action (mechanical activation).

With the 2D Lennard-Jones model, it was shown that after the homogenous formation of dislocations the system came to the quasi-stationary plastic flow conditions. The plastic flow goes on with the decomposition of the initial structure into blocks with the dimensions about 20-30 interatomic distances. The atom displacement in these blocks is correlated. The external energy loaded on to the solid released in the local regions in the form of the structure disruptions (dislocations) and in the form of the heat by dislocations in motion. The mean atomic kinetic energy field around the dislocation in motion is outlined. The heat trace of the sound velocity dislocation is observed within the range about 6-8 interatomic distances, the mean kinetic energy of the atoms in the trace is 50% larger than that in the whole system. The dynamic equilibrium between the external disordering action and the internal structure-relaxation processes is established in the model. Relaxation time is about 10-10 sec.

The ionic AB<sub>2</sub>O<sub>3</sub> model contains large anions and cations forming close packing, and small cations placed in the holes of the packing of large ones. It was shown that the large cations in the process of the deformation repulse with releasing the local atomic relaxation motion which causes the local structural reconstruction. These reconstructions form disordered regions between the blocks conserving initial structure. This kind of division of the initial system into two parts, with disordered and conserved initial structure, makes the relaxation of total stress field in the model more easy that lowering total energy.

On the 3D Lennard-Jones models we have analyzed the characteristics of the atomic space placement using the Voronoi-Deloneau methodology. We present the comparison of the liquid, supercooled amorphous solid, and the solid at the stage of the plastic flow, obtained with the help of our model.

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### Mechanochemical transformations of betulin and ursolic acid

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Betulin and ursolic acid were chosen as the objects of the investigations. Betulin is one of the mostly widespread triterpenoid and one of the compound constituting birch tree timber. To date this compound is forming in amount of thousands tons as undesirable side product of timberchemical industry, but from the other side is considering as perspective raw material for synthesis of valuable derivatives.

Ursolic acid belonging to the class of triterpenic acids is the component of the extracts of vegetable nature. Ursolic acid and betulin have very poor solubility in the most organic solvents, that makes very problematic their further conversion with traditional synthetic methods of organic chemistry. The object of this work is to study the transformation of above-mentioned compounds to valuable derivatives upon mechanochemical activation.

As oxidizers K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, oxygen systems MnO<sub>2</sub>, N<sub>2</sub>O-Fe<sub>2</sub>O<sub>3</sub> were used. Primarily we investigated oxidation of powders of ursolic acid and betulin at mechanochemical activation. Upon these conditions multicomponent systems, where individual compounds are very difficultly to analyze, is forming.

The oxidation of ursolic acid and betulin with the oxygen MnO<sub>2</sub> systems, hydrogen peroxide in liquid phase at mechanochemical activation was studied as well. Four main products are extracted and identified. The structures of identified products of the oxidation are depicted below.

Products structure was clarified with using IR spectroscopy, NMR <sup>1</sup>H, <sup>13</sup>C and XRD.  
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STUDY OF MECHANOCHEMICAL CONVERSIONS OF OIL COMPONENTS  
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The processes intended to manufacture the following oil products: motor gasolines, diesel fuels, and lubricating oils require complex equipment and a high energy consumption. There exists a must to develop effective and ecologically friendly small-sized alternative technologies based on non-thermal methods for activation of chemical reactions that proceed during the preparation of oil products. Mechanical action, being the most commercially accessible method for non-thermal activation of chemical reactions, as compared to other methods, would allow improving the production efficiency due to simple equipment and operation. At the same time the application of small-sized mechanochemical reactors in petrochemicals processes will allow to put into practice somewhat pure technologies. The aim of the present paper is to study possible mechanochemical conversions of individual oil hydrocarbons and oil fractions.

Mechanochemical treatment was carried out at room temperature on a centrifugal-planetary mill of AGO-2 type providing the acceleration of affecting bodies equal to 80 g. Steel balls 8 mm in diameter were used as affecting bodies. It was studied the influence of mechanical activation on the conversion of main oil components: n-alkanes with different number of carbon atoms in a molecule, cyclohexane, aromatic hydrocarbons with 1-3 condensed aromatic rings containing a various number of alkyl substitutes at different positions of aromatic rings. Gasolines and oil fractions taken within 200-450 °C at a step of 50 °C were subjected to mechanoactivation. The experiments were carried out both in the presence of catalytic systems that are traditionally used in oil processing and in their absence.

The occurrence of mechanochemical reactions is evidenced by the presence of hydrocarbons that were absent in the initial object of the study in the products. The degree of initial hydrocarbon conversion depends on its nature, the number of carbon atoms in a molecule, and the length of the hydrocarbon chain. The product yield and selectivity depend on the catalyst nature and modification, ratio between solid and liquid phases.

The occurrence of chemical reactions at room temperature under mechanical action may be explained as follows: 1) "quasiautoclave" conditions are created providing for a local increase in pressure and temperature (sufficient, e.g., to carry out alkanes isomerization);

2) the catalyst is activated at the appearance of the exits of extended defects in a crystal structure on crystal faces, as well as to the generation of newly formed surfaces with a great amounts of unsaturated bonds and an immediate participation of defects in hydrocarbon conversion.

#### **Amorphous and crystal structures of the products of mechanical alloying and leaching in the Co-Al system**

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The combination of mechanical alloying of metal aluminides with chemical leaching is promising for the preparation of 3d- metal phases with unusual structural, magnetic and catalytic properties.

The goal of the present paper is the investigation of phase composition of the mechanochemical alloys in the system Co-Al within concentration range 28-50 at.% Co, (where leaching is possible), and Raney Co catalysts that are prepared from this system. The equilibrium alloy with 28-50 at.% Co contains the phases Co<sub>2</sub>Al<sub>5</sub> and CoAl; the phase CoAl has the homogeneity range 47-50 at.% Co. In the case of the equilibrium alloy, Raney Co catalyst is formed during the leaching of the Co<sub>2</sub>Al<sub>5</sub> phase.

According to X-ray phase analysis data, only one crystal phase CoAl is formed by mechanical alloying in the system Co-Al within the studied concentration range. The lattice parameter of this phase remains unchanged with increasing Al concentration; it is 0.286±0.002 nm. According to the data of the transmittance electron microscopy, the alloy of the composition Co<sub>33</sub>Al<sub>67</sub> is an amorphous matrix with nanocrystal particles of the CoAl phase. This alloy was investigated by means of differential dissolving that allows to determine chemical composition of phases both in the crystal and in amorphous state. Two phases with the ratio Co:Al equal to 1:1 and 1:2,5 were showed up. So, along with the crystal phase CoAl, amorphous phase Co<sub>2</sub>Al<sub>5</sub> is formed in the mechanochemical alloys of the system Co-Al (28-50 at.% Co). Quantitative relations for the contents of these phases have been obtained.

The leaching of the alloys of this composition results in the formation of nominal amorphous cobalt with aluminum oxide physically included in the leached specimens. The amorphous phase Co<sub>2</sub>Al<sub>5</sub> is responsible for this process. X-ray phase analysis of leaching products points to the presence of the phase with the CoAl structure. The CoAl phase, as chemically more stable one, is likely to be partially retained in the structure of the leached alloy.

#### **Mechanochemical interaction in metal systems T.F. Grigorieva**

Mechanochemical synthesis in metal systems allows to receive both intermetallic compounds and solid solutions within concentration limits of equilibrium state diagram and non-equilibrium phases with nanometric grain size. Investigations of mechanochemical interaction in metal systems showed that this process passed in some stages and depended on the parameters of initial metals. At the stage of mixing of starting components, the reduction of size with the formation of layered composite nano-sized structures occurs. In these structures, close contact exists between the initial components that ensures very large area of its contiguity. The formed non-equilibrium structures have an excessive free energy because of high concentration of inter-grained boundaries. Thermo-mechanical characteristics of initial metals influence the first stage of the mechanochemical process. The mixing enthalpy of components plays an important role in the further activation. Nano-sized intermetallic compounds with maximum content of fusible or plastic component are formed at the second stage of mechanochemical synthesis in the systems with the negative mixing enthalpies. The amount of intermetallic compounds is increasing simultaneously with decreasing the amount of more fusible or more plastic components. Kinetic characteristics of the formation of intermetallics correlate with mixing enthalpies. The formation of solid solution is the mechanochemical dissolving of these intermetallics in solvent metal. The resulting supersaturated solid solutions have a highly imperfect crystal structure. Despite the sufficiently large particle size (~ 100 nm) the long-range order in the metastable phases persists only within 12-15 nm. The microstructure of the solid solutions is well described by a model taking into account the major types of the structural alloy imperfections: second-order microstrains and deformation stacking faults. With increasing synthesis time the structural perfection of the alloys improves: according to electron microscopy data the microstrain distribution becomes more uniform.

Mechanical alloying of high reactivity  
intermetallic compounds

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The reactivity of solid phase materials is the primary problem of solid state chemistry. High reactive metal powders are broadly used in industry (hydrogen storage materials, Raney catalysts, precursors of refractory materials etc). It is known that the reactivity of solid substances depends on concentrations and types of defects. Mechanical treatment of metal systems generates high concentrations of various defects such as interphase or intergrain boundaries, dislocations, disclinations, and allows to create non-stoichiometric defects. These defects allow to increase the reactivity of metal phases. Concentration and main types of defects change during mechanochemical synthesis. Investigation showed that the formation of supersaturated solid solution occurred in several stages. At the mixing stage the initial powdered metals form layered composite structures. The formation of nano-sized intermetallics in these layered composites takes place in the systems with negative mixing enthalpies. The formation of solid solutions begins with mechanochemical dissolving of these intermetallics in a solvent metal. According to TEM results, the main types of defects are second-order microstrains and deformation stacking faults. The microstrains are distributed over the volume of the isolated alloy particle very uniformly. With increasing synthesis time the structural perfection of the alloys improves: according to electron microscopy data, the microstrain distribution becomes more uniform. At the different stages of mechanical activation, the reactivity of products is investigated for the reaction with liquid gallium eutectics. Maximum reaction rate was achieved for the product at the beginning of the dissolution of intermetallic compound in solvent metal.

## Mechanochemical basis of the technology of cosmetic materials

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Traditional technology of the production of solid decorative cosmetic materials is based on separate milling of initial components, followed by mixing in ball mills. This technology is multistep and allows to use only the biologically inert materials as initial components, as far as it is impossible, using this method, to achieve highly homogenous distribution of the components, in which molecules are bound by hydrogen bonds.

Mechanochemical approach allows to simplify considerably the technology of production of the decorative cosmetic material and to create a material for medical cosmetics with decorative properties. Mechanochemical reaction of the neutralization of hydroxo-groups, appearing on surfaces of layered silicates under mechanical activation, by protons of biologically active materials, is the basis for the mechanochemical technology of the production of medical cosmetics. Interaction of the natural layered silicates with biologically active substances takes a short time. The rate of this mechanochemical reaction depends on the activation conditions. New materials for solid decorative, medical, and medical with decorative properties cosmetics were created using the same equipment.

MechanOCHEMical synthesis of dispersion composites  
with biologically active substances

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The research of mechanochemical interaction of natural layered silicates (talc, kaolinite) with various biologically active substances (BAS) (acids, salts, alcohols) is conducted.

It is established that, irrespective of natures of the investigated BAS, silicate hydroxo-groups are replaced with the anions of organic acids or alcohols. As a result, dispersed layered composites were formed. The natural silicate plays a role of the carrier, and BAS are chemically bound to it. This interaction is completed within 1-5 min for all the investigated systems. The examples of mechanochemical interaction in the systems: ascorbic + succinic acids; chitosan succinate with layered silicates demonstrate the possibility to obtain the medical preparations and biologically active food additives by means of mechanochemistry.

## Structural state of TiNi based alloy after mechanical activation

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The achievement of technology and investigations of TiNi based shape memory alloys characterized by the super fine and ultra-fine substructures (UFP), the fine-regulated porosity, high-strength and plastic are considered as the perspective scientific branch in our time. The powdery TiNi are broadly used in practice. The investigations of mechanically activated powder from TiNi based alloys are important for application aims. The results of experimental structure studies of mechanically activated TiNi UFP are presented in this report.

Such USP were prepared by mechanical activation (MA) of technical TiNi PN55T45 powder using the MPV grinding. The volume of steel drum is about 103 cm<sup>3</sup>. The ball diameters are about 0,3 – 0,4 cm. The relations of ball masses to the mass of initial powder (m) were the next: 5:1; 10:1; 20:1. The process duration is varied from 1 to 30 minutes. The structural analysis was carried out using the X-ray diffractometers DRON-2M and DRON-3M, which had been supplied, by thermal chamber with work temperatures from 140 K to 370 K.

The initial PN55T45 technical powder contains a cubic B2 TiNi phase and a small volume fraction (about 8%) of TiNi<sub>3</sub> and Ti<sub>2</sub>Ni type-like structure phases. It is the most possible that this phase was Ti<sub>4</sub>Ni<sub>2</sub>(N, O). The characteristic dimensions of particles are from 10 to 45 μm. The martensitic transformations (MT) B2→R→B19' are partially observed on cooling of powder (R and B19' are rhombohedral and monoclinic martensitic phases). The start temperatures of B2→R and R→B19 MT were about 200 K and 150 K, correspondingly.

It is shown that the increasing of stored energy, which is characterized by m, and the duration of MA lead to the increasing the volume fraction of particles which dimensions are less than 1 μm and it's simultaneous agglomeration.

The results of X-ray analysis show that the wide diffuse-like reflection is only observed in the vicinity of (110) B2 phase positions on diffraction patterns (DP) from powder after milling during 10-15 minutes. This is a result of both the increasing the volume fraction of UFP and the effect of their intensive plastic deformation. There is no changes of DP in

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temperature range from 150 K to 570 K. Therefore, stabilization of cubic B2 phase is observed after MA. The bright reflection of TiNi<sub>3</sub>, TiNi and Ti<sub>3</sub>Ni<sub>4</sub> phases are observed on DP of samples after weak compaction and thermal sintering of activated powder. The volume fraction of Ti<sub>4</sub>Ni<sub>2</sub> (N, O) phase is more less than in initial state of PN55Ti45 powder. The TiNi R martensite is observed in sintered samples at room temperature. The impotent role of stabilization of B2 cubic structure for the suppressing of aftereffect in sintered samples is discussed. In conclusion, the MA of TiNi in normal atmospheric conditions is analyzed. The displacement of maxim of diffuse-like reflection is observed to the positions, which characterize the TiNi<sub>3</sub> phase. It may be the indicator of an interaction between TiNi and an atmospheric oxygen. It leads to the TiNi instability due to the formation of titanium oxides. The increasing of supersaturation of B2 TiNi by Ni leads to the formation of TiNi<sub>3</sub> phase. Thus, the MA of TiNi must be carried out in screening medium.

### Mechanochemistry of Layered Double Hydroxides

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Layered double hydroxides are the compounds with the chemical formula  $[M(II)(1-X)M(III)X(OH)_2]Y^+(An-Y/n) \cdot mH_2O$  (LDH-A), where M(II) are the cations of double-charged metals (Mg<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, etc.) and lithium, M(III) are the cations of triple-charged metals (Al<sup>3+</sup>, Fe<sup>3+</sup>, Ga<sup>3+</sup>, V<sup>3+</sup>, Cr<sup>3+</sup>), and An- are interlayer anions. These compounds are widely used as precursors to obtain acid-base catalysts, sorbents, drugs, as well as anion exchange matrices of the "anionic clay" type [1-3]. The structure of LDH-A is formed by alternating charged layers  $[M(II)(1-X)M(III)X(OH)_2]Y^+$  and the layers containing A- anions and water molecules [4]. One of the most well known methods to obtain LDH is based on their precipitation from solutions containing the mixtures of M(II) and M(III) salts [1,3]. Co-precipitation method is connected with the formation of large amount of wastes. This method gives in most cases poorly crystallized, finely dispersed products. The preparations synthesized in this way are contaminated by uncontrolled impurities – most importantly carbonate ions – which bring substantial complications to the studies of their physicochemical properties. Because of this, the development of novel methods for the synthesis of LDH is undoubtedly of interest. One of the possible way of solving this problem is connected with using of mechanochemical methods. The data obtained are the evidence of the fact that the joint mechanical activation of magnesium (nickel) hydroxides with aluminium salts leads to the formation of layered double hydroxides with various anions. The proposed mechanochemical method of synthesis of the anion forms of LDH possesses a series of advantages in comparison with the traditional method of co-precipitation from the solution.

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### MECHANICAL ACTIVATION IN A1A2BO3 PEROVSKITE SYNTHESIS FOR OXIDATION CATALYTIC PROCESSES

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Mixed oxides of transition and rare-earth metals possessing perovskite structure (La<sub>1-x</sub>Me<sub>1</sub>xMe<sub>2</sub>O<sub>3</sub>, Me<sub>1</sub> = Sr, Ca, Ba..., Me<sub>2</sub> = Mn, Co, Ni, Fe, Cu) appear to be suitable for high-temperature processes such as catalytic combustion, methane reforming, ammonia oxidation, sulfur dioxide reduction, etc. due to their well-known thermal stability in a broad range of oxygen partial pressures and resistance to catalytic poisons. Recent progress in the development of methods and equipment for the mechanical activation (MA) of solids has opened a new way in the field of the catalysts preparation. The most apparent advantage of this method is the absence of waste waters, that is very important from the ecological point of view. The other attractive point is the energy saving due to decrease of the temperature and duration of calcination required to obtain a final product. As a consequence, it becomes possible to prepare complex oxides possessing a high specific surface and reactivity. As a rule, samples calcined at low temperatures have more disordered structure than those sintered at high temperatures, that may affect the catalytic properties of oxides.



This work considers the effect of the mechanochemical preparation method as compared with the traditional ceramic route on the phase composition, real structure and catalytic properties of perovskites ( $\text{La}_{1-x}\text{Me}_x\text{Me}_2\text{O}_3$ ,  $\text{Me}_1=\text{Sr}$ ,  $\text{Ca}$ ,  $\text{Me}_2=\text{Mn}$ ,  $\text{Co}$ ,  $\text{Fe}$ ) in the reactions of CO and hydrocarbons oxidation.

XRD, TEM, TA, BET, SIMS, SAXS, FTIRS, chemical phase analysis (CPA) were used for samples characterization. Catalytic activity in the reactions of CO, CH<sub>4</sub> and C<sub>4</sub>H<sub>10</sub> oxidation in an excess of oxygen was determined with the GC analysis.

The main feature of the MA route is formation of disordered nanophases already during MA of the precursors mixture. In the general case, disordered perovskite prepared by the MA method is characterized by a lower specific catalytic activity as compared with ceramic samples. However, due to higher specific surface area, activity per unit weight of perovskite is higher for samples prepared via MA route. In some cases, due to segregation of more active transition metal oxides on the surface, the MA product could demonstrate even higher specific catalytic activity.

#### INFLUENCE OF THE ULTRACENTRIFUGAL MECHANOACTIVATOR OPERATING PARAMETERS ON MECHANICAL ACTIVATION OF MICA POWDER

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Mechanical activation micas have a wide application in production of new materials, due to their physico-mechanical and physico-chemical characteristics. They can be used as fillers, coating and powders. Mechanical activation of mica is a great technological-technical problem because of their specific crystallochemical structure. The effects of mechanical activation depend on type of equipment used and the type of disintegration process.

In this paper, where the investigation of kinetics of mechanical activation of mica in ultra-centrifugal mechanoactivators with a peripheral comminution path was chosen as a programme task, were the general suppositions and conditions of the kinetics of comminution. Beside that, the investigation task can be reduced, in short, to the following: a detailed investigation of kinetics of a mechanical activation of mica in ultra-centrifugal mechanoactivators, of an advanced construction, with a peripheral comminution path.

Through a detailed investigation of kinetics of mechanical activation of mica, the elements for determination of the efficiency of ultra-centrifugal mechanoactivator with a peripheral comminution path were obtained, thus satisfying the requirements for definition of both technological parameters of mechanical activation and parameters of mechanical activation products.

On the basis of the investigation of these parameters and theoretical consideration of kinetics of mechanical activation in a mechanoactivator of advanced construction, by use of the contemporary instrumental techniques for determination and observation of the most significant physical, chemical and thermal characteristics, the kinetics model was produced to serve as the basis for quick and efficient determination of the parameters mention above, in order to optimize and automate the process of mechanical activation.

In this paper, the results of mechanical activation in ultra-centrifugal mechanoactivator Retsch ZM-1 were analysed.

#### SIMULATION OF PROCESSES OF SHOCK SYNTHESIS OF ALUMINIDES IN Ti-AI TYPE POWDER SYSTEMS

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The shock synthesis of aluminides allows to combine the technological processes of preliminary compressing of powder medium, activation of components and initialization of chemical transformations. It is essential, that the processes of synthesis of materials in mixtures with a high extent of activation can occur in a condition of solid-state reaction. Thus ultra dispersion nature of a compact and its structure are formed. The model of a reacting powder body, which is taking into account the presence of macroscopic structure of concentration inhomogeneity in powder mixture, is applied. The structure of concentration inhomogeneity always forms in mixtures of components with different sizes, density and physical-mechanical characteristics. Within the physical model the nonlinear bound problem of modification of powder medium by shock impulse, heat and mass transfer and macrokinetics of chemical transmutations is solved. It is supposed, that the shock effect can be submitted by macroscopic flat impulse of a loading, that reduce the problem to simulation of mechanochemical processes in reacting layer, introduced by sequence of elements of concentration inhomogeneity structure. The evolution of a mechanical state of powder medium at the front of shock impulse is modeled from positions of a mechanics of porous mediums with engaging of modified Nesterenko model. The modification consists in the taking into account of exothermic effects of chemical transformations. The change of reactivity of mixture caused by plastic deforming of components, fracture of surface layers of particles, and also resizing of structural elements during shock collapse of pores is considered. The results of a numerical modeling testify to an essential role of a local microstructure of mixture in a vicinity of points of elements of macrostructure on realization of different mechanisms of shock synthesis of aluminides and conditions of mechanochemical processes. Accessible degree of activation is defined by structure of concentration inhomogeneity of mixture together with intensity of shock impulse.

#### THERMALLY INDUCED PHASE TRANSITIONS IN MECHANICALLY ALLOYED Ni<sub>80</sub>Ta<sub>20</sub> AND Ni<sub>80</sub>Nb<sub>20</sub>.



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The kinetics and mechanism of the thermal relaxation of mechanically activated mixtures of Ni<sub>80</sub>Ta<sub>20</sub> and Ni<sub>80</sub>Nb<sub>20</sub> were analyzed by DSC and XRD. The powdery mixtures of the initial components were mechanically treated in an Ar atmosphere on a SPEX-8000 mill. As the dose of mechanical treatment increases, a solid solution of tantalum and niobium in nickel was first formed and then an amorphous phase [1].

At the final stage of the mechanical treatment, the Ni<sub>80</sub>Ta<sub>20</sub> system was amorphous-crystalline and consisted of an amorphous phase and a supersaturated Ni(Ta) solid solution with a composition close to that of the initial mixture. When the mixture is heated in the calorimeter, it exhibits an exothermic effect within 500-550 °C associated with the crystallization of the amorphous phase to a metastable  $\xi$ -phase containing 21 at. % Ta. The effective activation energy was found to be about 2.5 eV. Note that the composition of the Ni(Ta) solid solution remains unchanged. Thus, the amorphous phase is polymorphously converted into the crystalline phase. The isothermal kinetics of crystallization was described by the Avrami equation with an exponent about 3, a value typical of polymorphous conversions.

The maximal dose of mechanical treatment of Ni<sub>80</sub>Nb<sub>20</sub> produced only the amorphous phase. In this case, the crystallization of the amorphous phase yields a metastable Ni<sub>3</sub>Nb (with structure DO<sub>3</sub>, 25 at% Nb) and a supersaturated solid solution Ni(15 at. % Nb). This process manifests itself through an exothermic effect at a temperature within 450-550 °C. At higher temperatures (550–700 °C), the system comes to equilibrium Ni<sub>3</sub>Nb and Ni<sub>8</sub>Nb phases.

The reasons why the routes of the thermal relaxation of the Ni/Ta and Ni/Nb similar systems differ were discussed.

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### **Effect of media of mechanical activation on phase composition of sintered SHS materials TiB<sub>2</sub>-Fe**

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Industrial demands stimulate the search for methods to improve physical mechanical properties of SHS materials, obtained by sintering of SHS products.

One of the methods is the use of mechanical activation which allows, along with intensification of technological processes, improving operation characteristics of materials being sintered.

Investigation showed that SHS powders TiB<sub>2</sub>-Fe, activated with SHS grinding, are successfully pressed without plasticizer, sintering temperature decreases by 100°C, sintering duration decreases from 60 to 40 minutes.

The most interesting results were obtained during mechanical activation of TiB<sub>2</sub>+Fe SHS powder with the addition of alloying additives Cr and Mo in petrol. New phase of complex composition, occupying 80% of total volume, appeared in the sintered samples

### **THE DISPERSITY OF POWDERS PREPARED BY MECHANICAL MILLING. THE ANALYSIS OF LIMITING MECHANISMS**

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There is a limit for any of the currently existing methods of powders preparation, hindering further milling. Of special importance in this connection are the dispersion methods providing multiparameter action on the material milled, with parameters capable of controllable variations in wide limits. The technique of mechanical activation (MA) in liquid organic environments with the admixture of surfactants is among these methods. As a result of multiple cyclic actions in the process of the MA-technique, the particles acquire nanocrystalline structure. The purpose of the present investigation is to clear up physico-chemical mechanisms which impose limitations on the possibility of infinitesimal milling by the MA-technique

The principle of the model is that not conventional dislocations formed by atoms bring forward plastic deformation in the analyzed materials but macrodislocations representing linear defects in a regular nanograin package. Mechanical action will force these dislocations into movement, actualizing plastic deformation at the expense of intergrain gliding. When these dislocations outcrop onto the external surface, steps must be formed on the particles. It is important that the height of these steps should be multiple to the nanograin average size, and this fact was investigated experimentally by AFM.

It is believed that in order the dislocation outcropped onto the surface with the formation of a step the work on creation of the additional boundary surface should be performed. At low surface tension this outcrop is easy, therefore the particles will practically be superplastic at rather high sizes. Otherwise, jamming and piling-up of macrodislocations will take place, that will result in the particle destruction.



## STRUCTURE OF SURFACE LAYERS AND CORROSION STABILITY OF FINELY DISPERSED IRON PREPARED BY MECHANICAL MILLING IN ORGANIC MEDIA

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In this work the structure of surface layers of finely dispersed particles prepared by milling carbonyl iron in the heptane medium, also, in the presence of surfactant - 0.3 wt % of oleic acid has been studied as well as their corrosion stability (CS) in a isotonic solution. The dispersity of powders increases with milling time ( $\tau$ ) from 300  $\mu\text{k}$  to 18-30  $\mu\text{k}$  in heptane to 4  $\mu\text{k}$  in the presense of surfactant.

The investigations have shown that CS of the powders prepared at  $\tau=1$  h in the presence of surfactant and without it, is lower than that of the initial carbonyl iron, which can be explained by the dispersity increase. Despite the decrease of particle sizes at  $\tau.>1$  h the growth of the powders CS is observed, especially at  $\tau>24$  h, which correlates with the carbide phase appearance. CS of the powders prepared in the presence of surfactant is higher. The reasons for these phenomena were cleared up by investigating the structure of surface layers forming in the process of milling by means of X-ray photoelectron spectroscopy (XPS).

It has been shown that Fe<sub>2</sub>O<sub>3</sub> and the complex organic compounds with iron as the central atom are included in composition of all the prepared powders. No oxygen is observed in the dispersion medium in the case of heptane. Hence, not during the mechanical milling process but while performing the XPS-analysis in the spectrometer chamber does presumably the formation of an oxide layer take place at the expense of the residual air oxygen. In the case of surfactant the formation and growth of an oxide layer proceeds directly in the process of particle preparation at the expense of the oxygen in composition of surfactant. Also, in the process of milling the layer of organic complex compounds is formed on the surface of particles but its composition depends on the surfactant presence.

To sum up, the appearance of iron carbides increases the powders CS. It is the layers of the iron oxide and complex organic compound that impart the increased corrosion stability to the powders prepared in the presence of surfactant with the oxide layer fulfilling the main function.

### Specific features of surface layer formation under mechanical activation of iron in liquid environments

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The physico-chemical structure of ultrathin surface layers (<10 nm) of finely dispersed iron particles obtained at different stages of mechanical activation (3-99 h treatment time) in liquid hydrocarbon environment (heptane) has been investigated; as well as in the presence of surfactants (0.3 wt % oleic acid).

Our previous investigations have demonstrated that average particle sizes decrease from 100  $\mu\text{m}$  to 30  $\mu\text{m}$  (in heptane) - 4  $\mu\text{m}$  (in a surfactant solution) with treatment time and the particles structure is nanocrystalline (grain size 20-5 nm) even after 1 h of treatment. In the process of mechanical activation the particles are saturated with carbon, oxygen and hydrogen atoms, their source being heptane and oleic acid. The admixture atoms are located in intergrain regions with the formation of solid solutions in bcc-iron and finely dispersed inclusions of poorly ordered carbide and oxide iron phases.

X-ray photoelectron spectroscopy (XPS) and Auger-spectroscopy (AES) have been used to study the organic layers forming on the particles surface.

The following conclusions have been drawn from XPS-data. Degradation of heptane and oleic acid takes place in the process of mechanical activation. The C-H, C-C, C-O-bonds break and metal organic complexes are formed at the interface. When particles are prepared in the presence of a surfactant the forming oxide layer is attributable to mechanical activation. The thickness of this layer increases with milling time. Exposure in air does not influence composition and thickness of an oxide layer but affects the organic layer structure in that the quantity of oxygen-containing groups increases. The formation of an oxide layer on the surface of particles prepared in heptane takes place after removing from a dispersion environment. The composition and thickness of the resultant oxide layer does not depend from mechanical treatment time. Exposure in air also produces no changes either in an oxide layer or in an organic coating. AFM investigation demonstrates that the surface layer structure formed during the milling in presence of surfactant is noticeably differ from volume. The grain size in volume is equal to 4 nm, while at the surface it amounts to 20-400 nm.

### Solid state dissolution of cellulose in N-methylmorpholine-N-oxide

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Ecologically friendly technological process based on the dissolution of wood cellulose in solvent of donor type N-methylmorpholine-N-oxide (MMO) is now under scope having the name of MMO-process. This is the real alternative to the widely used Viscose technology of different materials and fibres.



The new solution of this problem is more profitable from economical and technological points of view. Instead of the general process of cellulose dissolution in liquid MMO, the solid-state interaction of cellulose with crystalline MMO is carried out under simultaneous action of mechanical shift and pressure on mixture system.

Under the conditions of all-around pressure, shift and induced plastic flux mechanochemical activation of cellulose and crystalline MMO take place. Initial processes of defect formation and amorphisation are determined and investigated. Physicochemical and structural investigations show that the solid-state reaction of complex formation occurs between cellulose and MMO. Calorimetric data suggest that the energy of H-complex formation is close to the energy of dissolution of cellulose in MMO melt. The conclusion is made about the route of dissolution of cellulose in MMO through the stage of H-complex formation. Under heating H-complexes are transformed to the fluent solutions. Properties, structural and phase transformations of these solutions are defined by the melting point of MMO used in the process, cellulose content of the mixture and the conditions of mechanical treatment. Possibilities to enhance special technological properties, such as the rate of fibre forming, technological flow-chart and special equipments are discussed.

### Mechanochemical methods of the formation of *n-p* transitions

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The review of mechanochemical approaches convenient for the formation of p-n transitions is the aim of this report based on the consideration of known physical and chemical effects taking place under intensive mechanical treatment of solids.

The disintegration of crystals and formation of defects of various types – defects of crystal and defects of crystallographic lattice - proceeds under mechanical treatment. Lattice defects play a major role in the formation of electronic properties of semiconductors. Mechanical treatment can be used to produce systems consisting of local zones with different types of conductivity.

Mechanical treatment of mixtures of solids leads to the formation of solid solutions. The dissolution occurs by nonthermal route as a result of ballistic diffusion or the movement of dislocations through interface. Effective diffusion coefficients are close in this case to those of the melts or solutions. Redistribution of phases takes place initially near the interface forming the zones with changed content and different electronic properties.

Mechanical treatment can form supersaturated solid solutions and nonequilibrium amorphous structures. Forthcoming annealing allows producing heterophase mixtures containing different types of conductivity. The peculiarity of this process is the appearance of ordered structure, which contains alternating regions of phases. From the point of view of theory of phase transformations, the mechanism of this process is opposite to the mechanism of random formation of nucleus of new phase, achievement of specific size and growth of nucleus. Consideration of the formation of ordered structures can be made in terms of spinodal decomposition theory. Probably this effect can be of interest for the formation of systems of ordered phases with different electronic properties.

Treatment of powder mixtures of substances with different plasticity forms numerous mechanochemical composites: particles of one substance are distributed in the matrix of another, layered composites, core composite with a layer of one component of the surface of the particles of another. Compacts from these powders can have nonlinear properties specific for p-n transition systems, for example, threshold effects in volt-ampere dependence.

Solid state mechanochemical reactions, for example, reduction of some metal oxides by another metal, lead to the nanocomposites consisting of the zones of reduced metal or of its lower oxide and zones of reducing metal.

*Formation of p-n transitions under mechanical treatment of silicon powder as a result of preferential introduction of defects to upper layer of particles.* It was shown for alkaline fluorides that the particles of limited size near 1 mkm are formed under mechanical treatment. More long-lasting treatment forms the upper layer on particle saturated by vacancies. The measurement of volt-ampere characteristics of silicon material of this type could be carried out. The blast compacting or another compacting method conserving defects in solids is necessary to prevent the disappearance of defects during compacting.

*Formation of p-n transitions due to mechanical doping and introduction of doping agent to upper layer of particles.* The change of conductivity type from n to p was discovered during mechanical doping of beta iron disilicide by boron. The sign of formed thermoelectric materials changed relatively. Possibly it is the result of the formation of disilicide particles with doping agents in upper layer.

*Formation of mixtures of phases with different conductivity types through relaxation of mechanochemically produced nonequilibrium states.* Solid state mechanochemical synthesis of molybdenum disilicide was investigated under intensive mechanical treatment of powder mixtures of molybdenum and silicon. The annealing of partially amorphous product of treatment gives rise to a mixture of molybdenum disilicide with lower molybdenum silicide having different types of conductivity. Diffraction of synchrotron irradiation with the spatial accuracy 5 mkm was used to study the distribution of products on the surface of molybdenum balls from mechanochemical reactor. The formation of multilayered structure was observed, the layer of the highest disilicide was localized in the upper part. Lower silicides were localized in deeper regions.

Another interesting peculiarity of the systems with different products formed during annealing of mechanochemically produced nonequilibrium state is irregular distribution of additives over phases.

*Mechanochemical production of core composites from the substances with different conductivity types.* Mechanochemical method of varistor production is developed on the basis of zinc oxide – bismuth oxide system. Covering of the surface of zinc oxides particles by bismuth oxide takes place under mechanical treatment of mixed powders. Compacted material has a threshold dependence of electric conductivity on voltage.

*Production of nanocomposites through mechanochemical reduction of oxides by metals.* The method is greatly used now for the production of nanocomposite materials. Real systems are defined now giving pairs of materials with different types of conductivity.



## Mechanochemical transformations of petroleum and brown coal in quasiautoclave regimes

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Chemical reactions characteristic for the elevated temperatures and pressures are observed in inorganic systems containing solid and liquid phases under mechanical treatment. The theory of this effect is based on the fact of the presence of gas bulbs in real pulp mixtures. Under the action of mechanical impulse on a definite region of pulp, the bulbs are compressed. Gas temperature rises and heat passes to neighbouring zones. Theoretical evaluation shows the possibility for micro zones to appear in which pressure impulse coexists with the temperature rise, so "quasi-autoclave" conditions are realized.

The obligatory condition for this effect is the hindered flux of liquid from the compressed zone as the result of the presence of solid particles there. The optimal volume ratio of water and a solid is determined to be close to 20 %.

Other approaches to the theory of this effect, for example, those based on the consideration of friction of particles in moving pulp flux are developing now.

The common processing of brown coals and petroleum may be effective from the economical point of view under specific conditions of Siberia, as low-level manufacture of products can be necessary for local consumption. The transport of materials for road construction and motor fuel to Yakutia is very expensive but there are local sources of petroleum and coals mainly of not very high quality. Specially developed technology consists of the joint mechanical treatment of mixtures of petroleum and brown coal in mechanochemical activator-mill and thermal extraction of light hydrocarbon fractions.

*The influence of mechanical treatment of brown coal/petroleum mixtures for the asphaltene formation.* Asphaltenes are the main component of road coverings, waterproofing films and upper roof layers. The fraction of Tolokan (Yakutia) petroleum after thermal extraction at 350 °C and brown coals of Kangalass (Yakutia) and Nazarovo (Kuzbass) were used as the initial raw materials. Asphaltenes and malthenes (petroleum oils and resins worsening the quality of road material) are determined in mechanochemical reaction products. Asphaltene content is shown to be maximal at petroleum/coal ratio 60/40. The malthene concentration is minimal under this condition. Possibly, there is a result of "quasi-autoclave" regime. The analysis of the contents of not only high but also low-molecular fractions with boiling point below 350 °C is necessary for the support of this thesis. The special equipment for the mechanochemical treatment of petroleum/oil mixtures with working volumes 25 and 320 liters is being tested now in Kangalass pilot usine (Yakutia).

*The influence of mechanochemical treatment of petroleum/coal mixtures on the formation of white hydrocarbon fractions.* Mechanical treatment of high temperature fraction of petroleum allows producing up to 10% excess of light fractions with maximal content of C20 hydrocarbons. Temperature rise leads to the decrease of light fraction yield. Distribution maximum moves from C20 to C22.

Mechanical activation of petroleum/coal 83/17 leads to the formation of the hydrocarbons of equal quality with distribution maximum C22 at all temperatures. Activation of 67/33 mixtures gives an unexpected result. The amount of hydrocarbons with lower molecular weight is increased. Hydrocarbons with C21 are formed to a maximal degree.

So, mechanochemical treatment of petroleum and its mixtures with coal leads to the formation of low-molecular products. The temperature elevation is a sufficient factor to enhance low-molecular fraction extraction from mixtures with great coal content. The possibility exists to increase the yield of white fraction up to 10%.

*Transformation of alkanes under intensive mechanical treatment.* Hydrocarbons of Talakan petroleum have normal structure, the fuels produced have octane index no more than 45. The possibility of the isomerization of normal alkanes under mechanical treatment was investigated. The fractions boiling at 33 – 219 °C and having octane index 43 were mechanically treated and the concentrations of hydrocarbons were measured. The treatment leads to the increase of C3 and C4 fractions to 0.2 – 1.7 mas% depending on conditions. The concentration of iso-structural C5 hydrocarbons increased to 1.2 – 1.9%. The changes of cycloalkane concentration were not substantial.

So, an increase of octane index by 1 – 2 points takes place under mechanical treatment. The use of autoclave regimes is a promising way for the application of this effect.

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## Low alkaline humate preparations: mechanochemical production, solubility and biological activity

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Humic acids are important part of brown coals, turfs and soils. Soluble salts of humic acids – humates - are produced through the reaction of humine-containing raw materials with alkaline solutions under elevated temperatures and pressures. Humic acids have different molecular masses and not all of them are useful from the point of view of living organisms. Low-molecular part of humic acids – fulvic acids – causes the largest biological effect. It accelerates the growth of plants. High-molecular part of humic acids has a blocking action on the agricultural animals' liver. So, separate extraction of low-molecular fraction of humic acids is promising. But it is difficult to do this through the reaction of solid with liquid alkaline because it is necessary to dissolve all humic acids, to separate high-molecular part by adding any mineral acid and to concentrate the fulvates.



Mechanochemical method of obtaining humates consists of mechanical treatment of humine-containing raw material with solid alkali. The structure of mechanochemically produced composite material contains distributed micron particles of raw and alkali. During the addition of water, microcomposite material eliminates the humates into solution.

The important peculiarity of this composite was discovered. If the concentration of alkali is not sufficient to dissolve all humic acids, low-molecular fulvinate part is extracted preferentially. So, it was not necessary to use high concentration of alkali to produce biologically active humate (fulvinate) preparations.

Chemical analysis of solutions produced by adding water to microcomposite materials with different alkali concentrations shows that the mechanochemically produced materials with lower alkali concentration leads to the formation of solutions with relatively higher concentration of fulvinate.

Biological activity of low-alkaline mechanochemically produced preparations is illustrated in experiments with cows at an agricultural farm.

## MECHANO-CHEMICAL EXTRACTION OF COPPER FROM ORE CONCENTRATES

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The concentrates of copper ores containing chalcopyrite, chalcocite, bornite are processed to the soluble copper salts through the treatment by water solutions of oxidizers. Generally iron (III) salts play a role of oxidizer. It is necessary to use the elevated temperature and pressure to extract the valuable components. The time of this leaching operation is measured by hours.

The application of mechanical treatment of concentrates allows to carry out the process under normal conditions. Preliminary mechanical treatment of solid - fine grinding - and mechanical treatment of pulps lead to the acceleration of leaching and to the decrease of leaching time down to tens of minutes.

The treatment of pulp is more effective than preliminary treatment of solid. Application of mechanochemical methods leads also to the increase of extraction degree. Positive results have been obtained in the processing of copper concentrates containing tetrahedrite from Central Europe, Slovakia and polymetal sulfides from Russia, Siberia, Norilsk.

The effect of mechanical treatment increases if high-energy activator-mills are used. The treating bodies of these mills are balls moving with acceleration more than 100 m/s<sup>2</sup>.

Another promising mechanochemical approach is the production of soluble complex ammonia copper salts through the mechanical treatment of solid mixtures of metal copper, copper (I), (II) compounds and ammonium salts. Oxygen of air plays a role of oxidizer in the process. At present, this unusual reaction is used for the recycling of copper-containing metal wastes.

The use of ammonium salts with low decomposition temperature gives rise to interesting technological perspectives. Decomposition of salt into gas ammonia and gas carbon dioxide is possible under mechanical treatment. Carbon dioxide under the conditions involved is in supercritical state. The drastic acceleration of diffusion of system's components is characteristic for supercritical conditions. Extraction rates of raw components can be increased by a factor of 10 - 100.

The possibility of solid-state formation of soluble copper salts from concentrates through mechanochemical processing of mixtures of copper concentrates with iron salts, ammonium salts and some additives is revived. The new technology includes only one main stage: mixing of concentrates with iron salts and/or ammonia salts and simultaneous chemical interaction under the treatment of mixture in the activator-mill. The dissolution of solid product in water allows to produce copper solution of maximal concentration and to separate insoluble sediment. The technology thus presented is ecologically friendly, characterized by minimal water consumption and can be applied now on the scale of up to 3000 kg of concentrates per hour.

### Application of mechanochemistry in hydrometallation reactions

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Various metal alkyls are used as co-catalysts of polymerization and reactants for fine organic synthesis. The most attractive methods for obtaining these metal alkyls are reactions of a metal with unsaturated hydrocarbons in hydrogen atmosphere, or reaction of hydrides with the same hydrocarbons. Such reactions are heterophase and are complicated because of mass transfer processes, inhibition by an oxide film and low reactivity of metals. All these complications are easily removed by the application of mechanochemical activation.

In the present work, mechanochemical method of active aluminium preparation was developed. Also the technique of preparation of aluminiumorganic derivatives from heptene-1 and dihydromercene was fulfilled. In the course of activation, aluminum doping by titanium and nickel was used to increase its reactivity. These metals catalyze reactions of aluminum with hydrogen and can adsorb atomic hydrogen with dissociation, which results in lowering the energy barrier for the formation of Al-H bond. This is necessary for hydroalumination. Aluminiumorganic derivatives of heptene-1, styrene and dihydromercene were obtained using this method.

The possibility to realize hydroalumination under the conditions of mechanochemical activation in drums of planetary mills was demonstrated for the first time. The mill API-2 was modified by replacing water-cooling system with a system of a heating with silicon oil and thermostat. After the oxidation of aluminum organic derivatives, the yield of citronellol with initial pressure of hydrogen 100 atm and temperature 850°Ñ was 65 %, and heptanol-1 under the same conditions - 60%. It is worth noting that mechanochemical reactions under such conditions have been carried out for the first time.



Butyl lithium was synthesized via the reaction of butene mixture with lithium hydride under the conditions of mechanochemical activation was synthesized.

These methods can be used as common ones to obtain organometallic compounds and find industrial application.

### The use of mechanical activation in analytical chemistry of difficulty soluble minerals

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Implementation of instrumental methods of analysis into modern analytical practice isn't always provided by the quality of probe preparation of the analyzed material. This problem is especially urgent when it is necessary to determine concentration of the elements on the 10<sup>-6</sup> – 10<sup>-7</sup>% level in the low-soluble compounds. Main requirements should be followed while conducting high-quality analysis of minerals and ores, which are: representativeness of sample and complete determination of analyzed elements from the matrix.

During geological sample preparation for the analysis, a number of difficulties arise, connected with the presence of difficulty soluble minerals, that are not decomposable when modern methods of sample preparation are used: high pressure and temperature, ultra-high frequency waves or microwave radiation, catalysis or highly aggressive chemical agents.

While determining trace contents of elements with non-uniform distribution in the matrix, we face the problem of probe representativeness. These problems could be solved by implementing the new age laboratory technique of decomposition. Implementation of the new kind of influence on the analyzed probe – mechanochemical activation – allows it to reach high level of homogenization and intensify the processes of chemical dissolution. In this case, not only the surface area increases, which provides better contact with chemical reagents, but it also leads to formation of highly active energetic states and defects of crystalline structure of the solid substances, which drastically raises the speed of dissolution.

Influence of mechanic forces leads to sufficient changes in the structure of analyzed materials. Being able to regulate these processes and understanding their mechanism is important in solving a number of analytical problems:

1. Increased level of homogenization of mineral probes and of their representativeness. In this case, fewer materials for analysis are needed.
2. Increasing speed of dissolution and decreasing level of concentration, used for analysis of reagents. The role of these factors is especially actual in decomposition of difficulty soluble compounds.
3. Intensification of connection between mineral surfaces and specific chemical reagents and formation of stable complexes as a result of initiation of highly energetic states in pre-surface layers of solid substances.
4. Energy changes in the structure lead to the drop of temperature, needed for fusion and agglomeration of samples.

For experimental confirmation of the use of mechanical activation in decomposition, research was conducted on oxides of titanium, tantalum, niobium, tin, and chromites. For intensification of decompositions during mechanical activation additions of inorganic salts (0,5 – 4%) were used. These additions intensify the dissolution effect, but they are destroyed and do not interfere in the analysis. Chloride and ammonium carbonate were chosen as the best additions. Introduction of ammonium chloride into the process of mechanical activation increases dissolution of chromite in hydrochloric acid by 7-8 times. X-ray analysis showed that the size of OKR blocks reduces from 800 to 100 .

The determination of concentration of platinum group elements in chromites was conducted with the use of two methods: fusion method with utilization of oxidizing agents, and mechanochemical activation method, with NH<sub>4</sub>Cl addition. It was shown that with the use of the suggested method the length of analysis becomes a few times shorter by omitting a series of labor consuming analytical procedures.

### SYNTHESIS OF FRAMEWORK COMPLEX ZIRCONIUM PHOSPHATES VIA MECHANOCHEMICAL ACTIVATION OF MIXED SOLID SALTS

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This presentation considers results of systematic studies of framework zirconium phosphates synthesis via mechanical activation (MA) of the mixture of solid salts followed by the hydrothermal treatment (HTT) of thus obtained precursors in the presence of surfactants, drying and calcination in air. Application of modern physical methods sensitive to the state of bulk and surface of nanosystems (XPD, SAXS, TEM, EXAFS, FTIRS, SIMS, UV-Vis) allowed to elucidate genesis of those complex systems containing different stabilizing/modifying cations and anions including NH<sub>4</sub><sup>+</sup>, K, Mn, Co, La, Al, Ce, V, Sb, W, F. For comparison, some systems were prepared via traditional sol-gel route.

The local structure of zirconium phosphate nuclei formed in the course of MA resembles that of layered zirconium phosphates. The spatial distribution of guest cations within those nanoparticles strongly depends on their nature as well as on anion composition of starting solid reagents, which determine a mode of the acid-base interaction in the activated mixture.



Moreover, the structural type of the crystalline by-product -ammonium salt affects properties of embedded zirconium phosphate nuclei as well. Those properties determine in turn realization of different mechanisms of complex framework phosphates crystallization under HTT -either via oriented stacking of primary particles (occurs even in neutral or alkaline solutions) or by dissolution-precipitation route (HTT in acid solutions). Subsequent annealing is accompanied by the lattice rearrangement due to removal of residual anions and cations migration within accessible positions. Factors determining the structural type, thermal stability, real/defect structure, surface composition and solubility of crystalline complex zirconium phosphates prepared via MA route were elucidated and analyzed as dependent upon the composition and genesis of those systems.

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## EFFECT OF MECHANICAL ACTIVATION ON PROPERTIES OF NON-TRADITIONAL CATALYSTS OF CYCLOHEXANOL CONVERSION

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Traditional resources for catalyst preparation are currently being exhausted and a search for new non-expensive materials is a goal of many studies. The idea to use industrial wastes as a source of raw materials is very attractive. In spite of common standpoint considering wastes as something useless they are materials already subjected to a primary treatment and very often a composition of wastes is close to a composition of traditional raw materials. However a direct use of wastes as catalyst components often fails because of a moderate activity of the resulted catalysts. This is the case for electrothermophosphorus slags - the wastes of phosphorus production by means of electrothermal technique. Mechanical activation seems to be a promising alternative for an improvement of the catalyst properties.

The electrothermophosphorus slags are glass materials consisting of calcium, magnesium, phosphorus oxides, silica and alumina. Copper-slag catalysts of cyclohexanol dehydrogenation were prepared by mixing of copper oxide with slag followed by reduction. Mechanical treatment of the mixtures in a high-energetic laboratory ball mill resulted in a dramatic growth of cyclohexanol conversion over the catalysts.

The  $^{27}\text{Al}$  NMR MAS spectrum of the initial slag as well as the spectrum of the untreated mixture consists of a single signal with the chemical shift of 51 ppm. This signal can be attributed to tetrahedral aluminum atoms. After a mechanical treatment no aluminum signals can be detected. This fact gives an evidence of a structural rearrangement of the slag matrix. Presumably a formation of aluminum atoms in low coordination take place, which leads to a significant broadening of aluminum line in spectra.

## THE DEVELOPMENT OF CEMENTLESS CORUNDUM CONCRETE TECHNOLOGY

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Among fundamental achievements in refractory technology during the last quarter of XX century, it is especially necessary to mark out the rapid rise of unshaped refractories' manufacture. This progress is caused forth basically by the development and integration of new kinds of castables of the types: low cement, ultra-low cement and cementless [1]. The latter class of castables does not contain any alien (with respect to refractory aggregate) binders. Abroad, the so-called reactive and tabular aluminas have found wide use as complex binders

In this work the following source materials were used when developing the technology of cementless concrete corundum composition:

As the refractory aggregate: fused corundum fr. 5-3, 3-1 and 1-0,1 mm. Specs. 3988-064-0224450-94. OSC "Alumina of Boxitogorsk".

As the finely dispersed matrix: fused corundum fr. 40-0 mcm, sintered corundum fr. 15-0 mcm and  $\alpha$ -alumina fr. 5-0 mcm. Specific surface of powders (according to the method of BET) was 1.5, 2.5 and 4.2 m<sup>2</sup>/g, correspondingly.

Finally, dispersed fuse and sintered diamond spars were obtained by vibratory milling followed by washing with hydrochloric acid from metallic iron. Gamma-alumina was dispersed in the air-stream mill with air separation. The blend was tempered with distilled water. The mix humidity was about 4,5%. The shaping of articles was carried out by vibratory casting. The raw concrete was exposed to firing at 12500C.

After firing, corundum articles had the following properties:

Open porosity, %	18,0
Apparent density, g/cm <sup>3</sup>	3,10
Compressive strength, MPa	72,0
Softening temperature under load, 0C	1700
Fraction of total mass, %	
Al <sub>2</sub> O <sub>3</sub>	99,0
SiO <sub>2</sub>	0,32
Fe <sub>2</sub> O <sub>3</sub>	0,09
Na <sub>2</sub> O	0,21

The developed technology requires subsequent improvement in view of lowering the temperature of thermal treatment of cementless concrete.



1. Yu. Pivinski. Ceramoconcretes – the final stage of lowcement castables evolution (part 1). Refractories and Engineering Ceramics. 2000. N 1. pp 11-15.

#### **Distribution of ligand field strength.**

**Generation by mechanical stressing, its consequences and technical application.** Mamoru SENNA *Faculty of Science and Technology, Keio University Hiyoshi, Yokohama, 223-8522, Japane-mail:senna@applc.keio.ac.jp*

Deformed molecules exhibit anomaly in various aspects. Mechanical stressing, being anisotropic in nature, on the molecular crystals inevitably brings about quenched deformation of constituent molecules. When we deal with coordination compounds, deformation of the molecule brings about disproportionation of ligands to change them into asymmetric, and hence develops distribution of ligand field strength. Consequences of introducing such asymmetry are very diverse. Gradual spin crossover and substitution of ligands by counter ions are only a few examples. Solid state ligand exchange is particularly of importance, since this opens up a new way for synthesizing various coordination compounds using neither solvents nor catalysts. Evidences of distribution of ligand field strength are shown for ferrous coordination compounds. Subsequently, application to the synthesis of some ferrous pyridyl compounds is shown.

#### **FORCE OF DECONDENSATION OF THE SUPERFICIAL LAYER OF LIQUID, SOLID AND GASEOUS SUBSTANCES**

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The author has developed the idea and applied it to the discovery of unknown fundamental force, which is called the force of decondensation of the superficial layer of water, in short FDSL. The essence of the force is as follows: water increases its surface when it flows along the boundary with another phase or in micropores; at this moment water layers, coming from depth to the surface, are decondensing with the force of temperature expansion for water as a whole (temperature component), and with force of osmotic pressure for the substances dissolved in water (osmotic component) (Shabalin, 1998, 1999, 2000).

This phenomenon helps to give new explanation of Rehbinder effect: surface-active substances assist only quicker permeability of water into sharp peaks of the joints extending during mechanical deformations. The water itself, at the expense of FDSL action, is decondensing and expanding with the force of temperature expansion, persisting to press the joints farther apart.

In author's opinion, FDSL manifests itself also during the formation of surfaces of solid and gaseous substances (Shabalin, 2001), and this is of great importance in mechanochemical technologies.

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Shabalin L.I. Force of Decondensation of the Superficial Layer of Water as a Fundamental Natural Phenomenon, Generating Exchange of Substances (claim for discovery). Novosibirsk, 2000, 155 p.

Shabalin L.I. Force of Decondensation of the Superficial Layer of Liquid, Solid and Gaseous Substances. Novosibirsk, 2001, 192 p.

#### **effect of HIGH pressure on the polymorphs of paracetamol**

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Effect of pressure on solid drugs is of great interest, because when processed many solid drugs are subjected to mechanical action and, in particular, to high pressure, for example when pellets are produced. It is important to know what can happen to a given polymorph during such a treatment, for example, if any phase transition is possible, in order to control the properties and bioavailability of drugs.

In the present study, effect of hydrostatic pressure on the two (I - monoclinic and II – orthorhombic) polymorphs of paracetamol was studied by X-ray diffraction in a diamond anvil cell at pressures up to 4.5 GPa (I) and 5.5 GPa (II).

The anisotropy of structural distortion of two polymorphs was well reproducible from sample to sample, also from powder sample to single crystal. The volume compressibility of the two polymorphs was shown to be practically the same. However, a noticeable qualitative difference in the anisotropy of structural distortion of the two polymorphs was observed: with increasing pressure the structure of polymorph II contracted in all the directions, whereas the structure of polymorph I expanded in some directions.

Pressure was also shown to induce polymorphic transitions between monoclinic and orthorhombic polymorphs of paracetamol. The transitions were poorly reproducible and depended strongly on the sample and on the procedure of increasing / decreasing pressure. No phase transitions were induced in the single crystals of the monoclinic polymorph at pressures at least up to 4 GPa, although a partial transformation of polymorph I into polymorph II was observed at increased pressure if a powder sample was used. It could be observed at pressure circa 1 GPa, when decreasing pressure slowly from a higher value. Polymorph II transformed partly into polymorph I during grinding. When increasing pressure up to circa 2

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GPa some new weak lines were observed in the powder diffraction pattern of the form II, which may be attributed to an unknown high-pressure polymorph of paracetamol.

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## INVESTIGATION OF THE STRAIN RELAXATION USING SYNCHROTRON RADIATION

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Previous works on solid-state synthesis of nickel tungstate have shown fast decrease of the width of initial powder peaks. It was decided to investigate its behavior during annealing. Synchrotron radiation, one-coordinate detector OD-3 and time-resolved diffraction technique were used for experiments on channel 5b of VEPP-3 (BINP SB RAS). The samples were mechanically activated for several time intervals. Then samples were put into furnace and the strain relaxation during annealing was investigated. Peak width was observed to decrease at the initial stage and then it increased slightly. We assumed this was related to the decreasing amount of defects (dislocations, for example) and then equilibrium state was achieved. The time of equilibrium establishment depends on temperature, so some kinetic parameters may be estimated.

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## PROSPECTS FOR MECHANO-THERMITE OPENING OF GEOLOGIC MATERIALS

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Traditional thermite and SHS processes for the production of various metals and nonmetal materials are widely known [1,2]. At present, the number of publications connected with the problems of initiation of combustive reactions in mechanochemical reactors rapidly increases. The interest to this problem is governed by the possibility of simultaneous conduction of several processes in a reactor, such as comminution-activation and the combustive reaction itself. Considerable experimental material has been accumulated and some applied aspects of these relatively new directions of investigation in mechanochemistry have been considered and summarized.

One of them is utilization of geologic materials (minerals, ores, concentrates) as one of the components of thermite mixture [3-6]. The possibilities of mechano-thermite process as applied to geologic materials is not restricted only to opening of "difficult" mineral raw materials (zircon, scheelite, columbite, pyrrhotine, etc.) but they can also be used in other applied and fundamental tasks: analytical (new method of conducting express-analysis of geologic samples), ecological (utilization of technogenic mining ore raw materials), technological (elaboration of new methods of production of constructional, refractory, ceramic and vitreous materials, noble metals and precious stones) and geological [7].

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### the effect of Mechanical activation on the formation of nanostructural niobium silicide during self-propagating high-temperature synthesis

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Mechanical activation (MA) is a promising method to intensify SHS in low-energy systems and obtain products with ultrafine structure. The effect of MA of niobium and silicon mixture in planetary mill on SHS, composition and structure of niobium silicides was investigated in the work.

As it was shown by X-ray phase analysis, the activation of mixture of niobium and silicon powders (Nb - 37,7 wt%, Si - 62,3 wt% - stoichiometry NbSi<sub>2</sub>) in argon for 2 minutes results in the formation of niobium silicides NbSi<sub>2</sub>, Nb<sub>3</sub>Si<sub>2</sub>, Nb<sub>5</sub>Si<sub>3</sub>, in this case the starting components are present in the amounts necessary for SH synthesis.

After 15 minutes of activation, the lines inherent to the main components are not observed in X-ray patterns. The intensity of silicide lines is maximal.



It was shown that 1-2 min MA of the mixtures of niobium and silicide powders (particle size  $< 5 \mu\text{m}$  and  $< 100 \mu\text{m}$ ), respectively, is necessary for the realization of SHS. The combustion temperature of the composition is 1600°C, which exceeds the eutectic point. Sizes of crystallites, determined according to Sheffer method, are from 400 to 850 Å.

Electron microscopy and X-ray phase analysis showed that plastic niobium is spread on silicon particles, forming agglomerates during MA. In this case silicide interlayers are formed at the interface of components.

Multiple grinding and the formation of agglomerates results in the creation of laminated agglomerates, consisting of their main components and silicides.

During SHS, the liquid phase of eutectic composition reacts with the main components and crystallizes, apparently, in very narrow zones, where the majority of crystallization centers exist as dispersed oxides and silicides being formed during mechano-chemical synthesis. The ultrafine structure is formed as a result of this processes in the after-burning zone.

## ON SOME POSSIBILITIES OF APPLICATION OF THE METHOD OF MECHANICAL ACTIVATION

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The original data on enhancement of capabilities of the mechanochemistry methods are considered based on the examples of activation of (1) sintering of heavy alloys, (2) the aluminium combustion process, and (3) synthesis of oxides of rare-earth elements.

The work demonstrates a common methodological approach: the combination of mechanical activation with the physical-chemical action of additives.

**1. Activation of sintering of W/Ni/Cu, W/Ni/Fe, and W/Ni/Co heavy alloys.** The mixtures of powders of the elements were subjected to mechanical treatment in inert atmosphere. Then, the powders were pressed at room temperature and were annealed. As a result, under the temperatures, which were below than in the case of the standard technology by 150–250 °C, the well-sintered samples of heavy alloys were obtained with the relative density of 99%. The optimal doses of mechanical treatment, the pressing conditions, and the composition of the samples, as well as their mechanical properties were analysed. The characteristic feature of the activated samples is a finer size of W grains as compared with the usual case. The main physical reasons of the sintering activation process are discussed.

**2. Activation of the aluminium oxidation processes.** Active aluminium was prepared on mechanical treatment of the mixture of aluminium with carbon in inert medium. The powders of active aluminium manifest activity in the oxidation reactions with water and oxygen. Interaction with water occurs totally already at the temperature of 50–70 °C and at higher temperatures, the reaction passes in the regime of heat self-acceleration. In air, behind the reflected shock wave, the ignition temperature of activated aluminium is below by 400 °C than the same temperature of ordinary aluminium with micrometer sizes of grains.

**3. Activation of the synthesis of Lu<sub>2</sub>Me<sub>2</sub>O<sub>7</sub>.** The combination of mechanical activation of the mixture of oxides Lu<sub>2</sub>O<sub>3</sub> + Me<sub>2</sub>O (Me = Ti, Zr, Hf) and their following heating made it possible to obtain complex oxides Lu<sub>2</sub>Me<sub>2</sub>O<sub>7</sub> with the pyrochlorine structure. For Me = Zr and Hf, the structures of such a type could not be synthesised by the other methods.

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## EFFECT OF MECHANICAL ACTIVATION ON PHASE TRANSFORMATIONS AND ELASTIC AFTEREFFECT OF TITANIUM NICKELIDE

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The functional porous permeable materials and constructions from TiNi-based alloys are applied in medicine for the substitution of tissue defects in the body. Self-propagating high-temperature synthesis (SHS) or powder metallurgy is used to obtain these materials. The significant volumetric growth of pressing porous materials takes place after pressing and sintering of TiNi powder. Such an effect is caused by high "elastic" aftereffect. Sharp anisotropy in the changes of the linear size of TiNi-cylindrical pressing samples is also observed. These features are stipulated by the reversible martensitic transformation (MT) beginning at the room temperature at once after the pressing load is removed and proceeding at heating. As a result, the gap of contact connections occurs between powder particles at the stage of volumetric growth. These features essentially hinder the creation of porous functional materials and constructions having the specific form for medical use.

In the present work we have investigated the influence of mechanical activation in planetary mill on the regularities of sintering of the TiNi-powder (technical grade PN55T45).

Mechanical activation was conducted in planetary mills with water cooling in petrol environment. The volume of steel drum was 1000 cm<sup>3</sup>, the diameter of steel balls was 0.3-0.4 cm, Mball/Mpowder - 5:1; 10:1 and 20:1, correspondingly. The duration of mechanical activation was selected in an interval from 1 to 30 min.

Pressing samples made from mechanical activated powders looked like cylinders with the initial porosity of 41-44%. For comparison, similar samples were prepared from initial powders. Pressing samples were sintered in vacuum 133·10<sup>-4</sup> Pa within the temperature range 1000-1170°C, for 2 h.



Volumetric growth was observed after pressing and sintering TiNi pressing powder not subjected to mechanical activation; it poorly decreased with temperature within the selected interval. The volume of cylindrical pressing samples of TiNi powder thus will increase by 18-20%, their diameter - by 2-2.5%, and height - by 14-15%. Sharp anisotropy of the changes of linear dimensions during sintering is caused by significant growth lasting in tuing the sintering of pressing samples of mechanically activated TiNi powder, instead of volumetric growth we observed shrinkage which is rather insignificant at temperatures 1000-1100oC and increases sharply at 1150 and 1170oC. The shrinkage continuously increases with increasing duration of mechanical effect. Anisotropy of the changes of the linear dimensions of pressing samples disappears almost completely.

The X-ray phase analysis (DRON-3, CuK $\alpha$ ) has shown that TiNi diffraction peaks broaden with increasing duration of mechanical effect. A rough estimate of the sizes of areas of coherent scattering under the Sherrer formula shows that the submicrocrystalline structure with the size of crystals approximately 10-25 nm is formed after mechanical effect within 5-30 minutes. The similar structure is formed after plastic deformation (more than 90%) which almost completely suppresses the MT.

Thus, the absence of the reversible MT and high-defect structure after mechanical effect sharply activates the sintering process, provides shrinkage of the TiNi powder pressed samples and eliminates the anisotropy of changes of the linear sizes almost completely. This allows to create functional porous medical implants possessing the specific form, dimensions and final porosity for the substitution of body tissues.

## CHANGES OF COMPOSITION AND PROPERTIES OF PeaTs DURING MECHANICAL ACTIVATION

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Variability of mechanochemical transformations makes it difficult to determine mechanisms and directions of transformations even for individual compounds; the problem becomes many times more difficult when the substance under mechanical activation is peat which contains a large class of chemical compounds whose chemical structure is only assumed.

Mechanical action initiates chemical transformations leading to qualitative and quantitative changes of the component composition of the organic substance of peat. Quantitative parameters of the changes depend on botanical composition and decomposition degree, duration of grinding and the accompanying medium, while the general trend of changes remains constant: the content of easily hydrolyzed and humic substances increases, while the yield of difficultly hydrolyzed and non-hydrolyzed compounds decreases. For water-soluble compounds, the changes varied from a two-fold decrease to the increase by a factor of 11.5.

The investigations prove reliable transformations of peat composition under the action of mechanical forces. For peat and humic acid (HA), the decrease of thermal stability was observed, along with the increase of hydrophobic properties, which is exhibited as the decrease of the amount of bound water.

Investigations of HA showed that the qualification indices are conserved when their yield increases, but chemical composition changes: the amount of methyl, methylene, alcohol and phenol groups increases, while the intensity of bands corresponding to carboxylic groups decreases; the amount of carboxylic groups decreases. Molecular mass distribution changes (increases or decreases, depending on the grinding medium).

Mechanical activation causes changes in the yield and characteristics of products obtained from peat (humic dye, rust modifier, stimulator of plant growth). This broadens the raw material basis of the production and improves the consumable properties of the products.

## AN EFFECT OF THE MILLING ENERGY PARAMETERS ON THE PHASE FORMATION RATE AT MECHANICAL ALLOYING OF BINARY SYSTEMS WITH POSITIVE (Cu-Cr) AND NEGATIVE (Fe-Mn) HEAT OF MIXING

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Phase formation processes at mechanical alloying of Fe<sub>50</sub>Mn<sub>50</sub> ÷ Ni<sub>50</sub>Cr<sub>50</sub> compositions were investigated. For Fe<sub>50</sub>Mn<sub>50</sub> composition, the time dependence of the fractional conversion was close to linear, whereas for Ni<sub>50</sub>Cr<sub>50</sub> composition this dependence possesses a parabolic shape. Moreover, aforementioned regularities were observed for various regimes of processing in planetary ball mill.

Obtained dependences were compared with the energy intensity and temperature of the ball milling process. Energy intensity and temperature were determined both theoretically and by experiments. It was shown that in general these two parameters are not proportional to each other. Effect of the energy intensity and the temperature on the mechanical alloying kinetics depends on the thermodynamic properties of alloying components. Fe-Mn system has a weak negative heat of mixing and for Fe<sub>50</sub>Mn<sub>50</sub> composition increasing both of the energy intensity and the temperature of milling results in the increasing of the phase transformation rate. On the contrary, Cu-Cr system has a positive heat of mixing and for Ni<sub>50</sub>Cr<sub>50</sub> composition we observed that increase in the energy intensity also led to an increase in the transformation rate, whereas the increase in the milling temperature results in the decreasing of the phase transformation rate.

Obtained results were discussed basing on the model of thermodynamic driving forces of the mechanical alloying process.

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**the Use of synchrotron radiation for *in situ* investigation of the physicochemical processes in solids under the influence of detonation and shock waves**

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During detonation of explosive materials (EM), very high pressure (million atmospheres) and temperature (thousands degrees) are realized. This gives a unique possibility for science to investigate the behaviour of a material under extreme conditions. Very interesting is the behaviour of the EM and other solids in detonation front.

The special instrumentation was developed for the investigation of explosion. This is an explosion chamber, detonation front sensors and position-sensitive detectors (PSD), which were synchronized with the movement of electrons in the VEPP-3. The explosion chamber now can operate with an amount of an explosive close to 50 g (the trotyl equivalent); this will be 200 g in the nearest future. It has an entrance window for the primary synchrotron radiation (SR) beam and exit windows for SAXS and WAXS [1].

Our team was the first in the world who used SR for the studies of the behaviour of the explosive material during detonation. We have obtained unique results: 1) information about the behaviour of density immediately after the front of detonations with time resolution of 250 ns was achieved; 2) new phenomenon was discovered - the appearance of the SAXS signal immediately after the detonation front; 3) SAXS signal for different explosives was explored with time resolution of 250 ns.

A set of experiments on the investigation of reactions in solids initiated by detonation (silver stearate, paraffin, teflon, Al powder) and by shock wave (copper ammonium perchlorate, nickel hexamine, paraffin, diamond powder) was carried out.

[1] B.P. Tolochko, N.Z. Lyakhov, et al. Nucl. Instr. Met. Phys. Res., 2001, v. 467-8, p. 161-164.

**MECHANOCHEMICAL PROBLEMS OF THE SYNTHESIS OF TITANATES**

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Synthesis of ceramic materials is intimately connected with the problem of formation of the required defective structure in starting powders. Methods of mechanochemical synthesis of nanostructural powders, being currently developed, are based on the elucidation of the nature of structural and chemical transformations occurring during mechanical treatment (MT) of powder mixtures.

In this work we present results of EPR and IR spectroscopy studies of evolution processes proceeding in oxide mixtures (ZnO-TiO<sub>2</sub>, BaO-TiO<sub>2</sub>) subjected to mechanical treatment in a vibratory mill with the aim of obtaining powders of titanates with a specified composition. The initial processes of macro- and microarrangement of the structure in individual components of the mixtures that are a prerequisite for further interphase transformations of oxides (ZnO + TiO<sub>2</sub> → ZnTiO<sub>2</sub>, BaO + TiO<sub>2</sub> → BaTiO<sub>3</sub>) were established. Along with grinding the components of the mixtures, a complex of defects exhibiting paramagnetic properties and used as «probes» of occurring changes forms.

An investigation of the kinetics of accumulation of paramagnetic centers with increasing time of MT made it possible to establish the influence of local pulse mechanochemical effects on the formation of the defective structure of the powders. Thus, the following two processes determine the process of interphase interaction during MT: accumulation of defects in the components and a significant increase (sufficient for a solid-state reaction to proceed) in the temperature of the mixtures.

**MECHANOCHEMICAL WAY OF CELLULOSE ESTERIFICATION**

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The original technology of obtaining fast-soluble solid disperse systems is developed at the Institute of Solid State Chemistry and Mechanochemistry. A number of medicinal forms of acetylsalicylic acid have been created on this basis. The rate of dissolution of such medicinal forms is much higher than that of individual substances, which promotes an increase of efficiency and decrease of undesirable by-effects. However, the synthesis of drugs with prolonged action is of great interest. One of the ways to solve this problem may be the synthesis of cellulose esters containing the functional groups of medicinal substance in the structure. The way of preparation of such substances in solution is complicated because of decomposition of cellulose esters in many organic solvents and their hydrolysis in water solutions.



The purpose of this work is the development of solid-phase mechanochemical way of synthesis of cellulose ester from cellulose and salicylic acid. Laboratory samples have been prepared by joint treatment of initial reagents in high-energy mills - activators with the subsequent washing out of excess reagents and by-products. The influence of the time of activation and additional treatment of cellulose by various alkalis is investigated with the purpose of increasing the replacement degree of cellulose hydroxyl groups. The obtained samples were studied by means of IR-spectroscopy, differential thermal analysis, X-Ray diffraction. The content of salicylates in samples was determined with the help of SF-46 spectrophotometer by analyzing the solution obtained as a result of complete hydrolysis of the sample. Under the conditions of sample preparation, this value achieved 12,3 % mass., which corresponded to replacement degree of 16,4 residues on 100 cellulose elementary units.

Thus, the opportunity to obtain cellulose salicylic ester by mechanochemical way is shown for the first time. Such researches are especially actual for the further application to various drugs and may be used as models to obtain drugs with prolonged action and gradual excretion of functional groups and prolonged soft therapeutic effect.

#### CONTRIBUTION OF MECHANIC ACTIVATION OF COAL TO THE DEVELOPMENT OF THEORY AND PRACTICAL ASPECTS OF ADVANCED COAL TECHNOLOGIES

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The paper presents the explanation of the effect of activation grinding in attrition mill in order to achieve favourable environmental and technological results. The effect of mill revolutions, grinding time, shot and concentration of leaching agent was studied in laboratory conditions during the mechanochemical grinding of brown coal from Nováky. In addition to surface-structural characteristics, the activation effect of grinding has been also evaluated on the basis of changes in the organic structure (CHO) of coal using CAPTO method. In order to improve the filtration parameters of fine-dispersed brown coal, the effect of concentration of alkaline agent was studied within the range of 5 – 0.1% weight. It was confirmed that favourable environmental (detoxification, desulphurization, reduction of contents of ash matters, etc.) and treatment (increase in the extraction of treated coal) effects were achieved under conditions of stable structure of humic acids. The target regulation of mechanochemical changes represents a potential possibility of this progressive mechanochemical method for the preparation of rare organic diterpene-based substances. These substances can be used as pharmaceutical effectors in production of medicaments. In relation to information published by the scientific mechanochemical school of Russian scientists, it is possible to expect that this mechanochemical procedure will have a more complex use in environmental areas.

#### MECHANOCHEMISTRY OF COAL

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The study presents information on mechanic activation of brown and bituminous coal. The effect of mechanic activation is evaluated by physical-chemical methods (NMR spectroscopy, DTA, CAPTO method, IR spectroscopy), as well as by surface-structural methods. In case of Slovak brown coal with relatively high contents of ash and As (average 600 ppm) and sulphur (more than 3%), it was managed to achieve a favourable effect in the organic structure of coal. C-13 and C-17 NMR spectra confirmed that mechanochemical changes cause different occurrence of organic compounds (various carbonaceous carboxyl, aldehydic and carboxyl groups, aromatic, alkaline and anomeric carbons and sp<sup>3</sup> carbons with bonds C-C, C-O, C-N, etc.). In case of evaluation of O-17 NMR spectra, it was only the water signal that was registered. IR spectra of mechanically activated brown coal in dry conditions and in planetary mono-mill pulverisette 6 confirmed that the effect of mechanochemical changes is different. DTA study of mechanochemically activated samples in dry conditions and in alkaline medium brought important information about the shift of endothermic peaks in temperature areas, which may have the consequent application use. In consent with the applied knowledge it was confirmed that mechanical activation in air medium causes a favourable oxidation of organic structure of coal, which leads to the increased contents of humic acids in organic structure of coal, similarly as in case of mechanochemical procedure in alkaline medium- GACL (Grinding and Aqueous Caustic Leachnig). Mechanochemical activation of coal in various activators represents a great advantage due to favourable environmental impact on the use of lower quality brown and bituminous coal.

#### MODELING OF COMBUSTION OF EXOTHERMIC COMPOSITES IN MECHANOCHEMICAL REACTORS

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Mechanically-induced self-propagating reactions (MSR) have been thoroughly studied during the recent years [1]. Experimental results on MSR under various treatment conditions have been reported for the system Sn-S-Zn [2]. The heat of the chemical reaction itself is important when calculating the heat sources at the impact-friction contacts between the particles under treatment in mechanochemical reactors. This effect was first taken into account in [3, 4].

The goal of the present report is to interpret and calculate the activation time before the ignition of the combustion reaction (the main parameter of MSR) for the system Sn-S-Zn in SPEX8000 mill. The considerations will be based on the following assumptions: a) at the beginning of the treatment, self-lining of the milling bodies takes place; b) sulphur, as the most pliable component, covers all metal surfaces uniformly; c) only sulphur undergoes profound structural changes (melting, amorphization, polymerization); d) the formation of metal sulphides takes place as a result of reactive diffusion of elements under the calculated t-P-T (time-pressure-temperature) conditions at the impact-friction contact between the treated particles.

The ignition of MSR occurs when a critical state is achieved due to mechanical activation. The following possibilities are concerned as the decisive parameter of the process: 1) a certain critical temperature is reached at the centre of metal particles; 2) a critical number of sulphide particles is formed gradually by continuous nucleation and growth, providing active sites where the combustion of the initial substances can start; 3) a critical total reaction surface area is reached.

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## MECHANISM OF MECHANOCHEMICAL SYNTHESIS FOR COMPLEX OXIDES

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Determination of mechanism of mechanochemical reactions first of all means to find primary factors determining dynamics of process. The primary factors can be defined by finding of linear dependence of the chemical response on mechanical loading. The complexity of a problem of determination of relation between mechanical loading and chemical response of a system is possible to present, as a *double black box*: the unknown process goes in a black box - very complex for the description the mechanical apparatus, for example, planetary mill. The achievement of understanding of complex process is impossible without elimination from consideration purely of apparatus. It was made by choice of identical conditions for mechanical treatment and variation of chemical systems  $MO+M'O_3$  with different physical parameters. The relative comparison of chemical response in the same type systems on identical mechanical loading does not depend on the choice of parameter of mechanical loading and way of description of the apparatus - black box. Therefore, for realization of calculations the mean impact of a ball in a flat non-dense layer of a powder was used. The product of mean impact energy on frequency gives mechanical energy, brought to a material. Best parameter of mechanical loading is a mean heating of a material in a zone of impact. The best parameter of the chemical response is a half-yield of product  $K=1/E1/2$  kg/MJ. Semi-transformation energy  $E1/2$  is the most exactly defined parameter of synthesis dynamics by XRD-method. Correct comparison of heating of a reactionary zone, which can be calculated only for the first act of loading, with a half-yield  $K=1/E1/2$  (i.e. after  $\sim 102$  acts) is possible in the case of a similarity kinetic curves that is really observed. The factor of linear correlation  $T\sim 1/E1/2$  is  $r=0,67$  for all systems with congruent character of melting for product  $MM'O_4$ . The account of an enthalpy,  $\Delta M$  ( $M$  - Mohs's hardness), deviation from crystal type stoichiometry and relative thermal conductivity improves a linear correlation up to  $r=0,9414$ . Linear dependence of the rate  $K^*$  on  $T^*$  and threshold effect testifies about *non-diffusion* character of process. In model for reactionary zone the formation of intermediate *dynamic state* (flat layer from voids and rollers - rotated atomic mixture of reactants) on a contact of particles at the moment of loading was offered. The observable product is a result of relaxation of *dynamic state* in conditions of quenching. Tailored preparation of nanosize powders of complex oxides is possible by use of the created model. 20 new compounds of complex oxides were obtained at last time. Crystal products of mechanochemical synthesis often have perovskite-, spinel-, sheelite-, pyrochlor-, fluorite- and rock salt-related structures.

## A SET OF NOVEL DEVICES FOR DRY PROCESSING OF POWDERS

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Few devices with option of separation, including based on mechanochemical phenomena, were designed for investigations and complex processing of dry powdered materials.

Title of device	Separation	Working range of	Possible operations	Possible capacity,
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	parameter	fineness		TPH
Electro-mass-classifier (EMC)	$\sim e/m$ , Mohs's hardness	20 nm – 3mm	Selective milling, activation, separation	$\leq 5$
Magnetic separator on FeNdB-magnets	$\sim \sigma/m$	20mcm – 1mm	Separation of para- and ferromagnetics	$\leq 0,5$ for 1m drum
Tribo-adhesion separator	$\sim q/m$	20mcm – 1mm	Separation on the sizes and charge	$\leq 0,5$ for 1m drum
Magnetic adhesion separator (MAS)	$\sim F(\sigma q)/m$	20mcm – 1mm	Separation of complex mixtures	$\leq 0,5$ for 1m drum
Magnetic photo-adhesion separator	$\sim F(\sigma q, D)/m$	20mcm – 1mm	Separation of complex mixtures, including a colour	$\leq 0,5$ for 1m drum
Vibrating table	$\sim \bar{n}$ , D, shape	20mcm – 1mm	Separation on size, gravity and shape	0,1-0,5 for 1 m <sup>2</sup> of table surface
Permanent sieve	$\sim D$	>100 mcm	Separation of coarse particles	$\leq 1$ for 1 m
Electric separator	$\sim F(\epsilon, q)/m$	20mcm – 1mm	Separation on conductivity	$\leq 1$ for 1 m

A set of devices allows to classify complex powdered materials and to determine an optimal route of its complex processing. A set of listed devices was successfully used for design of next dry and semi-dry technologies: refinement of kaolin and glass sand, utilization of fly ash as a binding material, utilization of granite dust for pozzolana, separation of metallurgic slakes, processing of CuMo-wastes of flotation, concentration of Cr-ores, separation of magnetite from fly ash, refinement of talc and marble for white fillers, etc.

### The study of mechanically activated complex sulfides transformation at long keeping

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Previous investigations have shown the long-time effect of iron sulfide mechanical activation. The oxidizing reactions initiated by power mechanical pulses were continuing after the end of the treatment practically up to the complete sulfide decomposition under the mild conditions. The generation of Fe<sup>3+</sup> ions (which are stronger than oxygen oxidizing agents) in molecular contact with the particles surface during activation and supported consequent phase transformation was shown to be the main reasons of this process.

The claim of the present investigation was to study the phase transformation of the mechanically activated complex non-ferrous metal and iron sulfides at long-time keeping in the closed to natural conditions. Different samples of pentlandite ((Fe,Ni)<sub>7</sub>S<sub>8</sub>) and chalcopirite (CuFeS<sub>2</sub>) were used as objects in dry, wet and mix mode experiments. The mechanical activation was performed in two steel 630 ml drums of centrifugal-satellite mill by stainless balls of 5 mm diameter. The samples were characterized by thermogravimetry, microscopy and X-ray diffraction.

At wet mode keeping of the pentlandite activated for 1 min the millerite (NiS) peaks have appeared and increased up to 80-90% of initial main phase. The pirrotite (Fe<sub>x</sub>S<sub>x+1</sub>) peaks have appeared during the first month too. During 10-12 months the complete decomposition of the starting sample has been reached. It can be supposed the solid state decomposition of complex sulfide goes to the simple ones. Due to intensive oxidizing of the new-formed pirrotite to the goethite (FeOOH), sulfur and iron sulfates (according the referred mechanism) the equilibrium will move to the decomposition products. The chalcopirite is more stable. Although blue copper sulfate salt deposits were observed on glass reactor vessel walls, a new phase formation was detected only at the mix mode keeping. The difference in behavior and obtaining compounds is connected with the different properties of secondary simple sulfides.

The results have demonstrated the long time effect of mechanical activation of sulfide minerals. It eliminates hard requirements on the activated apparatus productivity capacity. Using oxidizing potential of atmosphere and hydrosphere the methods of the non-reagent treatment of sulfide concentrates in keeping place closed to geotechnological ones – with minimal expense and decreasing of technogenoes pressure on environment – can be developed.

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### Abrasive materials and instruments made of mechanically activated corundum

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The production of abrasive materials and instruments remains one of large-scale application areas for powders varying in composition and structure. One of modern directions of its development implies the creation of hardware exhibiting at the same time high level of properties and their stability, which is especially important for finishing operations of processing.

The goal of the present work was the investigation of the effect of mechanical activation on the properties of abrasive grains and instruments manufactured using ceramic binder. This type of binder is used for instruments operating



under severe conditions. Its manufacture is based on difficultly controllable liquid-phase agglomeration processes developing in the subsurface layers of abrasive grains and causing worsening of performance characteristics. Unlike traditional approaches, the application of mechanical activation allows directly influencing the formation of inter-grain boundaries and the properties of instrument.

The subject of investigation was corundum abrasive materials used at many stages of processing. Vibratory (VM) and planetary centrifugal mills (PCM) were used for mechanical activation.

The measurement of abrasive ability with respect to K 8 glass revealed differences in the changes of the parameter with changing the grain size in usual and activated states, and the effect of activation conditions. At the initial stage of activation, when mainly dispersing of particles is observed, along with disordering in the subsurface layer, the abrasive ability is practically the same for the materials with different grain size in non-activated and activated states. The accumulation of defects in small grains during activation in VM and PCM in air decreases the abrasive ability, while for usual materials it increases due to the increase of the total area of cutting edges. Aggregation processes have no effect of abrasive ability. When activated in the vapor of liquid nitrogen in VM, the change of abrasive ability with grain size is similar to the usual case, though variation coefficient becomes more stable. The data obtained are not in contradiction with the existing notion of activation and dispersing processes. Initial stages of activation are likely to be promising for technological application. Abrasive powder obtained under these conditions was used in high-speed honing instruments. Industrial tests demonstrated high performance characteristics of the instrument and the possibility to use it instead of imported analogues.

The effect of mechanical activation of filler on the properties of fireproofing composition

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Measures providing fire prevention are still actual in modern society. Fires cause deaths and injuries, bring substantial economic and ecological hazard. One of efficient means to provide fire prevention is to treat the surfaces of materials and constructions with swelling fire-protective compositions.

The goal of the present work was to study the effect of mechanical activation of the filler on the properties of fire-protective composition based on silicate binder. ZnO, Al<sub>2</sub>O<sub>3</sub>, MgO and SiO<sub>2</sub>, substances exhibiting basic, amphoteric and acid properties, were used as filler. Activation was carried out in a planetary centrifugal mill with  $g = 40$  in air and in water.

The major performance characteristics of the composition – swelling (an increase of the volume of protective layer) and adhesion to the surface depend on the type of filler and on mechanical activation in different manners. The type of filler and its activation have only insignificant effect on swelling of the coating. Adhesion is more sensitive to the type of state of filler. The most high-strength coating was obtained using Al<sub>2</sub>O<sub>3</sub> in the form of alumina composed mainly of  $\alpha$ - and  $\gamma$ -modifications as a filler. The use of mechanically activated alumina causes an increase of adhesion from 1.88 to 2.55 MPa. The data of granulometric analysis demonstrated that the maximum effect was observed with fine disperse powder that has not reached the aggregation stage or that has passed to the stage of desaggregation. The result is somewhat worse with the composition based on Al<sub>2</sub>O<sub>3</sub> in  $\alpha$ -modification. No effect of activation medium on the properties of coating was observed. By means of complete factor experiment, a physicochemical model has been developed to optimize the parameters of composition, state, and properties of the composition. Technological process has been developed.

The composition has passes the State Certifying Tests and licensing. Experimental production is organized at the industrial basis of the Joint-Stock Company “Corund”. The use of mechanically activated filler in the composition caused an increase of the warranted performance lifetime of the coating by a factor of 5-6, compared to analogues.

### **Technological processes of the production of materials on the basis of mechanically activated powders**

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Technological application of mechanically activated particles is one of the directions of priority in modern material science. The goal of the present work was generalization of the information obtained by the author in the area of investigations into physicochemical foundations of the use of mechanically activated powders in the production of a wide range of powder composite materials.

It becomes possible to solve the problems related to the reliability of materials operating under extremal conditions by providing the required level of parameters for phase composition, size of structural fragments, status of phase and structural boundaries, status of crystal lattice. The technologies of obtaining materials should control diffusion processes and structural phase transformations at the microscopic level. In this sense, the use of active particles allows one creating new diffusion channels, directed changing of the size of phase fragments, forming optimal states of their boundaries. A profound rearrangement of the structure and deformations accompanying these processes, as well as structural strain caused by them, are spread over the whole particle volume or its substantial part, eliminating the differences in the state of atoms near the interfaces and far from them. High surface energy of boundaries provides the development of self-organization effects in structural fragments directed at filling crystal planes most densely populated with atoms. The decrease of the difference between structural energy states of atoms in the surface regions and within the volume of the particle causes an increase in the diffusion mobility and lowers the energy barriers. Model investigations and technological tests allowed revealing the most appropriate structural schemes of the status of activated particles of the necessary functional destination. A real technological process is one of the combinations of processes leading to obtaining these schemes realized at the conversions of the preparation of mixture components.



The developed technology of activating powder systems of functional destination was introduced when obtaining a group of composite refractory materials, special coatings, abrasive and cutting instruments, technical ceramics including the reactor ceramics.

***Special refractory materials based on mechanically activated fillers***

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The production of refractory materials remains one of large-scale application areas for the powders of various composition and structure. Modern direction of the production of refractory materials, which involves obtaining the hardware by molding plastic masses based on fillers and binders, appears to be the most promising direction for the application of mechanochemical technologies.

The goal of the present work was the investigation of the effect of mechanical activation of fillers on the technological regimes of the process, composition of binder and properties of refractory materials obtained by molding mixtures of concrete and slurries. Unlike traditional approaches, mechanical activation allows direct influence on the status of intergrain boundaries formed during the interaction of sub-surface layers of filler with chemically active binder and determining the performance behaviour of hardware.

The subject of investigation was corundum mass used in industry and based on phosphate binders. Vibratory (VM) and planetary centrifugal mills (PCM) were used for mechanical activation. In vibratory mill, the process was carried out in air, in the vapour of liquid nitrogen and in water, the amplitude of vibrations being 1.5 mm and frequency 50 Hz. Activation in PCM was carried out at in air and water.

The kinetic investigations of the interaction between the components of the binder with the filler demonstrated that mechanical activation in gas media accelerates the process by increasing the pre-exponential factor in the Arrhenius equation. The powder activated in water interacts with the binder similarly to the initial powder. The increase in rate is proportional to the increase of contact area between phases. No effect of the changes in the parameters of the microstructure of powder at different stages of activation was observed.

By means of complete factor experiment, a physicochemical model optimizing the parameters of composition, status and properties of the obtained materials has been developed. Technological process has been developed and experimental production has been established. The practice of the industrial application of the hardware at the apparatus of titanium-magnesium production at the Joint-Stock Company <UK TMK> demonstrated the high reliability. The operation lifetime increased by a factor of 70 for some hardware operating under severe conditions.

Mechanochemical way of changing a sorption activity of zeolites on the example of natural chabasite

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Zeolites, owing to their unique physicochemical properties including molecular-sieve effect, high sorption, ion-exchange, and catalytic capabilities, are widely used worldwide. In general, synthetic zeolites are used, however, the range and scale of their application is primarily controlled by their high cost.

As a possible alternative to synthetic minerals, the adsorption properties of natural zeolite-chabasite have been studied. This zeolite differs from other minerals of that class by large-volume cavities and comparatively high thermal stability.

A comparative analysis of the adsorption parameters of the synthetic and natural zeolites shows that with respect to such substances as water and CO<sub>2</sub> vapors the above mentioned properties have similar values while with respect to others, specifically, benzol vapor, the natural chabasite ranks considerably below synthetic analogue.

To increase a sorption capability of the natural chabasite, a mechanochemical activation has been applied. The adsorption properties were studied under the static and dynamic conditions. The adsorption capacity for water vapors under static conditions has been determined by the desiccator technique at a relative partial water vapor pressure  $p/p_0 = 0.1$  and 0.6. Benzol adsorption was carried out at  $p/p_0 = 1$ . Carbon dioxide adsorption capacity under static conditions has been calculated from the adsorption isotherms.

It was shown that the adsorption capability of separated chabasite with respect to the substances investigated (CO<sub>2</sub>, H<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>) changes ambiguously. While adsorption of water and carbon dioxide vapors decreases as time increase, the adsorption of benzol vapors increases from 3.5 % for the initial sample to 11.7 % for the activated one.

The rise of adsorption activity during benzol adsorption indicates that a secondary porosity of mechanically activated chabasite increases as the diameter of a benzol molecule ( $d=0.63 \mu\text{M}$ ) is larger than a window size of a natural chabasite ( $d=0.37 \mu\text{M}$ ). However, a decrease in adsorption of H<sub>2</sub>O and CO<sub>2</sub> vapors, which are adsorbed within micropores, points to deformation of the crystalline structure and associated destruction of the channel system of a sorbent.

The experiments on air sorption-desorption (the latter process was carried out at 20°C and 400°C) showed that preliminary mechanical activation results in an increase in a quantity of strongly adsorbed air. The obtained experimental data point to a possibility of intensification of the adsorption processes occurring in mechanically activated chabasites, which is determined not only by change of the pore sizes but also formation of the active centers at zeolite surfaces.

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**CHANGES IN CHEMICAL COMPOSITION OF PEATS**



## DURING MECHANOCHEMICAL ACTIVATION

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The initiation of chemical transformations of peat by mechanical methods is a poorly explored but a promising field of researches as far as concerns the development of novel technologies. The degree of structural changes of peat components depends on the type of mechanical action and feedstock nature.

Mechanical activation of peat and its mixtures with various reactants was carried out in a vibrocentrifugal mill. Sphagnum and wood peat were subjected to mechanochemical dispersion in the presence of alkali and celoviridine. Lipid fractions, water-soluble (WS) fractions and humic acids (HA) were extracted from the peat activated.

The influence of mechanochemical activation on the yield of fractions, their composition and structure depending on the peat species was studied. It was shown that the yield of WS fractions increases by 5-20 times, that of HA – by 2-3 times. A maximum increase in HA content was observed at mechanical dispersion and activation in the presence of celoviridine due to the destruction of hard-to-hydrolyze substances (HHS). On peat activation in alkali presence, the WS content increases as a result of HA and HHS hydrolysis. The yield of lipid fractions from activated peat in all the modes of mechanochemical activation decreases as compared to the initial peat. An assumption on the processes of peat transformation during mechanochemical activation was made on the basis of elemental analysis. H/C atom ratio in peat subjected to mechanical dispersion decreases, and increases by the contrast, in the peat activated in alkali presence. In the first case it points to the processes of compaction of peat components, and to the destruction processes in the second case. The occurrence of oxidative processes is observed only at alkali excess.

The distribution of functional groups by lipid, WS, and HA fractions evidences different directions of mechanochemical transformations in peats of different types. In lipid and WS fractions of sphagnum peat the decrease in the content of active functional groups is observed, whereas their content in HA increases. In similar fractions of the wood peat an opposite picture is observed: the content of functional groups drops in HA and increases in lipids and WS.

## MAGNETISM AND STRUCTURE OF NANOPARTICLES

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At present, much attention is attracted to the investigations of the dimensional dependence of the magnetic properties of nanoparticles and microclusters. Magnetic effects connected with the finite size become prevailing for the particles of several nanometers in size. Besides the known phenomenon of superparamagnetism, fluctuations of exchange interactions appear on the surface as a result of distortions of coordination and symmetry; the fluctuations cause, for example, the formation of surface non-collinear structures. The dependence of main magnetic parameters, such as saturation magnetization, Curie temperature, anisotropic constant turn out to be the functions of dimensions. The problem of inheriting or changing magnetic properties and structure of particles while the cluster size increases becomes principal.

For the clusters with decreased number of atoms (tens and hundreds of atoms – the species of this kind are sometimes called mesoscopic), along with classical features, substantial are quantum phenomena causing spin transformation of magnetic structure, both with decreasing size and with posing external magnetic field.

Clusters containing d- or f- ions (V15, Mn12, Ac, Fe6, Fe8, Fe10, etc.) are now extensively investigated. Relatively weak interaction between clusters in these molecular crystals allows to investigate quantum regularities and the changes of magnetization of individual isolated clusters.

The present report will present modern analysis of magnetic properties and structure of nanoparticles and microclusters and description of the major achievements and new results including both literature data and original experimental results in this area. Anomalous magnetic features will also be considered (the parameters of hysteresis loop, susceptibility, spin configurations, etc.) in ferro- and antiferro-magnetics (Ni, NiO, CuO, etc.) in the nanophase state synthesized by different procedures (gas-phase, mechanical grinding, etc.).

The report will include the results on unusual behaviour in strong magnetic field (up to 40 T) of low-temperature magnetization of cobalt and iron clusters in non-magnetic copper matrix.

The above-mentioned phenomena are undoubtedly of interest not only for the understanding of fundamental problems of magnetism but also provide substantial outlooks for practical application.

### **Influence of the milling bodies contamination on the results of mechanical alloying Fe and Si(C) powder mixtures**

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In the results published concerning the mechanism and sequence of solid state reactions on mechanical alloying there are often considerable differences. We believe, one of the reasons for these differences can be contamination of the sample ground by the material of the milling balls and vial and participation of the wear product in mechanical alloying.



In this report we present the results of studying powder mixtures Fe(68)/Si(32), Fe(75)/Si(25) and Fe(68)/C(32) ground in planetary ball mills Pulverisette-6 and Pulverisette-7 with the balls and vials made of WC, stainless steel (12% Cr + 8% Ni) and hardened steel (1% C + 1.5% Cr). Mechanical treatment was carried out in an inert atmosphere (Ar). Getting of milling bodies material into the sample studied was monitored by the mass of the vials, balls and powder before and after the treatment. It has been ascertained for all types of the milling bodies that increasing the powder mass can achieve 20% at long grinding time, corresponding to the formation of the supersaturated solid solution.

It has been shown by X-ray diffraction, Mössbauer spectroscopy and magnetic measurements that the least wear resistant and more inclined to participate in mechanical alloying material is stainless steel. Thus, in most cases it cannot be used in studying solid state reactions requiring mechanical treatment for a long time. For this purpose the most suitable material is hardened steel with high wear resistance. The main advantage of WC is the fact, that being present in the sample milled it does not take part in mechanical alloying.

The work has been supported by the Russian Foundation for Basic Research (projects No. 00-03-32555, 01-02-96463).

### **MECHANICALLY ALLOYED BINARY Fe-X (X=C, Si, Ge, Sn): KINETICS, THERMODYNAMICS AND MECHANISM OF MIXING**

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Common and distinctive features of mechanical alloying of Fe with sp-elements in atomic ratios 68:32 and 75:25 have been established by the methods of Mössbauer spectroscopy, X-ray diffraction, magnetic measurements and thermodynamic calculations within the Miedema's model.

Among common regularities we have found the following: the formation of a nanostructure state in  $\alpha$ -Fe at the initial stage and sp-element penetration along the  $\alpha$ -Fe grain boundaries; the formation of sp-element segregation and first Fe-M phase in the interface region (boundary and close-to-boundary distorted zone); the realization of any type of solid state reactions on reaching the nanostructure state; the condition of supersaturated solid solution formation on reaching some critical grain size in the interval  $< 10$  nm.

The following should be attributed to the differences: sp-atoms (Si, Ge, Sn) having approximately equal and substantially larger size in comparison with Fe with an equal sequence of solid state reactions have different kinetics of reactions with Fe; C atom of a small radius results in differences in the sequence of reactions as well. In alloying  $\alpha$ -Fe with Si (Ge, Sn) at the first stage the most stable for the given binary systems intermetallic compounds are formed in interface regions. At the final stage supersaturated solid solutions (SSS) are formed in the grain bulk. In the Fe-Si system SSS formation of Fe(Si) is characterized by a slower kinetics in comparison with that for SSS of Fe(Sn) in the Fe-Sn system. However, in the Fe-Si system the Si concentration in SSS becomes maximum practically simultaneously with the SSS formation, meanwhile in the Fe-Sn system SSS is saturated with Sn gradually. In contrast to the Fe-Si and Fe-Sn systems in  $\alpha$ -Fe alloying with C at the initial stage in interface regions either supersaturated solid solution or amorphous phase is formed. The growth of C concentration in its with the time increase of the mechanical treatment results in the formation of the Fe<sub>3</sub>C carbide with subsequent absorption of non-reacted  $\alpha$ -Fe and C by it, the initial atomic ratio being 75:25. With the ratio 68:32 the transition of Fe<sub>3</sub>C into Fe<sub>7</sub>C<sub>3</sub> is observed.

The work has been supported by the Russian Fund for Basic Research (project 00-03-32555).

### **Investigation of chemical and structural transformations of chitin and chitosan in solid-phase carboxymethylation using mechanical activation**

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Investigation, development and introduction of the technologies involving chitin, chitosan and their derivatives are among the most important achievements both in chemistry and in pharmacy. Practically inexhaustible resources and unique properties of these natural biological polymers provide their universal part in various areas of human activities and serve as the starting point of the search for new areas of their application. One of the promising directions is obtaining carboxymethyl esters of chitin and chitosan. The solubility in water broadens the possibilities of their application. The goal of the present study is the investigation of the effect of mechanical treatment on the initial compounds, solid-phase synthesis of the carboxymethyl esters of chitin and chitosan.

X-ray phase analysis of the initial compounds and mechanically activated samples demonstrated that these compounds are materials with low degree of crystallinity. Mechanical activation resulted in the increase of the intensity of X-ray lines of chitin, which can be the evidence of the re-crystallization of amorphous phase, while mechanical treatment of chitosan caused amorphization of the substance

Carboxymethylation of chitin and chitosan has been carried out with the help of mechanical activation. It is demonstrated that an increase of the time of mechanical treatment causes an increase of the transformation degree of functional groups in chitin and chitosan, which leads to the increased solubility of these derivatives in water. Relative viscosity of the solutions of these products decreases only insignificantly with increasing synthesis time



IR spectroscopic investigations revealed that mechanical treatment of chitin in alkaline medium results in the decrease of the intensity of the band in the region 3270-3300  $\text{cm}^{-1}$ , which corresponds to the stretching vibrations of NH group of chitin. This can be the evidence of partial deacylation of chitin.

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## THE EFFECT OF MECHANICAL ACTIVATION ON THE STRUCTURE AND REACTIVITY OF RICE HUSKS

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In recent years the processing of vegetable raw materials without a preparatory separation into individual components is becoming a prevailing subject of research. The use of mechanochemical activation of vegetable materials promotes their subsequent modification aimed to obtain water-soluble products based on cheap and ecologically harmless initial substances.

The effect of mechanical activation on the structure of rice husks – cellulose-containing vegetable product – is considered. One carried out mechanical treatment of the product using a laboratory microgrinder of a planetary type MA-1. The time of mechanical treatment varied from 1 to 30 minutes. Based on data of a microphotographic analysis it has been shown that the size of particles in the samples of mechanically treated rice husks changed from 1 to 50  $\mu\text{m}$ . The maximum grinding of the substance, characterized by average size of the particles, is achieved if the time of mechanical treatment is 3 minutes. In this case the average size of particles accounts for 3.3  $\mu\text{m}$ . One can observe substance grinding only up to a certain moment. Prolonged grinding, when the time of mechanical treatment of the product is more than 8 minutes, promotes particle enlarging and aggregation. Recrystallization is supposed to proceed, which is supported by the data on the presence of free radicals in the samples of mechanically-activated rice husks.

In accordance with the study performed the time required for sufficient substance grinding may be considered as optimal time for preliminary activation of rice husks. At present stage when aggregation of separate fragments does not occur yet it is easier to carry out the followed substitution reactions. The substitution is carried out to modify cellulose components of rice husks and to obtain soluble products.

At present the data obtained are used to study reactivity of rice husks in alkylation reactions. They may be also useful to develop novel polymer compounds based on cellulose-containing materials via mechanochemical treatment.

## THE APPLICATION OF MECHANOCHEMICAL TECHNOLOGIES IN ZEOLITE CATALYSIS

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Catalytic activity of high-silica ZSM-5 zeolites in the chemical reactions is due both to their molecular-sieve and acidic properties. One of the possible ways for their control is the mechanochemical activation (MCA) of a zeolite. By varying the time and the intensity of the action on the catalyst one may directly change its physicochemical, adsorption and catalytic properties. In this connection the goal of the present work was to study the influence of the mechanochemical activation on ZSM-5 properties.

For investigation purposes we used a zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3=60$ ) produced under hydrothermal conditions from alkali aluminosilicagels and decationized by 25 %  $\text{NH}_4\text{Cl}$  solution. MCA treatment of the sample was carried out in a centrifugal planetary mill at the operating load of 80 g. Steel balls of 8 mm in diameter were used as milling bodies. To carry out MCA of a sample a ball vibrating mill was also used. Owing to different mechanical actions, zeolite treatment period changed from 5 to 20 min in the planetary mill and from 24 to 96 hours in the ball vibrating mill. The crystallinity degree of ZSM-5 activated was calculated using IR-spectra, their specific surface was measured using chromatography by low-temperature argon adsorption. The acidic catalyst properties were studied using temperature-programmed desorption of ammonia. The catalytic activity of the samples was studied in the process of conversion of different hydrocarbons. The reaction products were analysed using gas chromatography.

MCA of a zeolite catalyst leads to the decrease in its crystallinity degree, specific surface and acidity. In the composition of the products obtained at the conversion of straight-run gasoline fractions on activated ZSM-5 the concentration of aromatic hydrocarbons decreases, the content of  $\text{N}^5+$  isoalkanes increases, the yield of the desired product increases. The activity and the stability of the catalyst operation in the aromatization of propane-butane fraction increase after MCA in the vibrating mill for 12 hours. The yield of arenes increases by almost 10 %, the service cycle – by 1.5-2 times. Thus, MCA application allows not only improving the methods for zeolite synthesis but also effectively change its performance.

## FUNDAMENTAL BASES OF MECHANOCHEMICAL TECHNOLOGIES FOR THE CHEMISTRY OF BORANES AND THEIR DERIVATIVES

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The chemistry of boron demonstrates many unique features that distinguish this element from any others. These special features of boron chemistry have led to a variety of applications of diverse boron compounds. Borohydrides (boranes) and their derivatives have various applications in technologies. Mechanical engineering, inorganic and organic syntheses, electronics, metallurgy, catalysis, technological processes of layer and coating deposition, paper industry and medicine are the fields in which borane derivatives are used or their application has been shown to be reasonable.

The subject of this work is application of mechanical activation (MA) of solids to some important objects of the boron hydride chemistry. We have shown the mechanochemical methods are very effective for synthesis of series of borane volatile derivatives and diborane(6) B<sub>2</sub>H<sub>6</sub>, [1,2]. The reactions were carried out by MA of the solid crystalline mixtures in the vacuum ball mills without using any organic solvents. The rotative and vibratory mechanical activators were used. Advantages of mechanochemical synthetic methods are : (a) the absence of solvents; (b) the preparation of products in sufficiently pure state ; (c) the increase of yields of products owing to elimination of some auxiliary operations; (d) environmental pollution with liquid wastes may be decreased. This work summarizes the results of studies of the following mechanochemical reactions :

1. The synthesis of B<sub>2</sub>H<sub>6</sub> from M\*BH<sub>4</sub> (M\* = Li; Na; K) and halides of polyvalent metals MX<sub>n</sub>.  
$$MX_n(s) + nM^*BH_4 \rightarrow B_2H_6(g) + H_2 + M + nM^*X; M = Cu; Zn; Sn; Pb; Cr; Cd; Ge; X \text{ is a haloid.}$$
  
$$SnCl_2(s) + 2M^*BH_4(s) = B_2H_6(g) + H_2(g) + Sn(s) + 2M^*Cl(s); \text{ the yields of } B_2H_6 \text{ are } 43 - 98\%.$$
  2. The synthesis of borane adducts with nitrogen-containing Lewis bases (L) of the type L.BH<sub>3</sub> .  
$$L.HCl(s) + M^*BH_4(s) = L.BH_3(\text{liq.}; g) + M^*Cl(s) + H_2(g). L = Me_3N; Et_3N; (C_7H_7)_3N; Py; N_2H_4.$$
  3. The synthesis of borazine H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>.  
$$3NH_4Cl(s) + 3M^*BH_4(s) = H_3B_3N_3H_3(g) + 3M^*Cl(s) + 9H_2(g); \text{ the yields are } 18 - 30\%.$$
  4. The synthesis of tetrahydroborates of transition metals M(BH<sub>4</sub>)<sub>4</sub>; M = Zr; Hf; U.  
$$MCl_4(s) + 4M^*BH_4(s) = M(BH_4)_4(\text{liq.}, g) + 4M^*Cl(s); M^* = Li; Na; \text{ the yields are } 35 - 95\%.$$
- The above-mentioned reactions may serve as a base for mechanochemical technologies.

[1] V.V. Volkov, K.G. Myakishev. *Inorganica Chim. Acta.* 289, No 1-2, 51 (1999).

[2] V.V. Volkov, K.G. Myakishev. *Chem. for Sustainable Development.* 7, 1 (1999), in Russian.

### Secondary Crystal Structure: New METHODS of APPROACH IN MECHANOCHEMISTRY

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New theory of secondary crystal structure (SCS) has been developed in [1-3] and some its applications have been presented. According to [1-3], a monocrystal consists of elementary units – mics (mic = minimal crystal; about 300 Å in size). Mic represents an analogue of the giant polymer (crystalline) molecule and contains 106 ÷ 108 atoms. An ordinary molecule that has lost an atom is a molecule-radical possessing enhanced reactivity. The crystalline particle less than mic in size constitutes a subcrystal – an analogue of molecule-radical. The subcrystal possesses increased specific energy due to a deficit of mass (or number of atoms) relative to that of mic. At that, mutual potential energy U of subcrystal atoms also increases. The additional force field arises from this as  $\frac{U}{r} = F$ , where F – force of atom bond, r – distance. Subcrystal becomes the center of attractive forces for the surrounding particles – the center of non-specific adsorption («an active center»). This conclusion is of fundamental importance for the solid state chemistry since the formation of «active centers» is the main way to control the reactivity of solids. Such centers (subcrystals) are created by different means: vapor condensation, etching of the surface or crystal volume, mechanical treatment (mechanochemistry). Subcrystal solid structures possess unusual and practically important properties: high energy saturation and reactivity of nanocrystalline materials, unusual properties of lamellar heterostructures («quantum points», «quantum wires»), porous crystals (silicon). Subcrystals on the surface of solid determine its adsorption and catalytic properties.

Under mechanochemical treatment of substance, subcrystals of different sizes (“crystalline radicals”) form at all times. According to SCS theory they possess increased free Gibbs energy G and high reactivity. Mutual contact of subcrystals of the same material results in their aggregation (“amorphisation”, “Beilby layer”). This restricts the limits of disintegration of solids [4]. At contact of subcrystals of different substances, their interaction is possible with the formation of new product (at appropriate ΔG of reaction, by analogy with Hedvall effect).

1. Yu.I. Vesnin *J. Struct. Chem.*, 36, N 4 (1995) 655.
2. Yu.I. Vesnin. *Secondary Structure and Properties of Crystals.* Published by the Siberian Branch of the RAS, Novosibirsk, 1997 (in Russian).
3. Yu.I. Vesnin. *Chemistry for Sustainable Development*, 8 (2000)129; <http://www-psb.ad-sbras.nsc.ru/csde.htm>
4. G.S. Khodakov. *Physics of Comminution.* Nauka, Moscow, 1972 (in Russian).

### Research of structure detonation nanodiamonds by a method of destruction in a planetary mill

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As is known, detonation nanodiamonds have a fractal structure. Having generated in process coalescence of particles of a liquid diamond phase by the size 4-6 nm, they form primary units by the size up to 20 nm, which are in turn used for formation of secondary structures. On the X-ray data and measurements of density, the assumption was stated, that the primary particles nanodiamonds can be hollow.



For finding out of morphology of particles nanodiamonds the study of changes texture and properties of nanodiamonds was undertaken at attempt of their crushing. The destruction of fractal structure nanodiamonds were carried out in a planetary mill APF-5M with steel balls and settlement acceleration - 60g; times of activation - 1,5 and 10 minutes; an atmosphere - air.

X-ray analysis has shown, that, since time of activation 5 min., were found reflections of a phase  $\alpha$ -Fe with  $d = 0,203; 0,143$  and  $0,117$  nm, which intensity a little bit has increased for a sample activated 10 min. At the same time intensity of reflections of a diamond phase practically has not changed, as well as half-width of these peaks. It testifies that mechanical activation has not changed microstructure of nanodiamonds, though the cases of broadening peaks owing to increase dispersion are more often known.

The activation of nanodiamonds a little bit reduces temperature of beginning oxidation and essentially reduces temperature of a maximum of oxidation of nanodiamonds.

As follows from data of analysis of evolution gas, activation significantly changes its content: with increase of time of activation the share of  $N_2$  and  $H_2$  grows, the share  $CO_2$  decreases, after 10 minutes of activation occurs  $CH_4$ , the quantities of  $CO$  and  $O_2$  vary insignificantly.

On base of these data it is possible to assume, that on the first stage were destroyed carboxyl groups and after that destroyed cavities between separate particles of diamonds.

HREM investigation didn't found any destroyed separate particle of nanodiamond.

Thus, it can be concluded that conditions which were used for mechanical activation of fractal nanodiamonds were effective for destroying of its fractal structure, but not separate particles.

### **THE EFFECT OF MECHANICAL TREATMENT ON THE PROPERTIES OF PIROXICAM AND its MIXTURES with $\beta$ -cyclodextrin**

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Mechanical activation of molecular crystals of drugs is known to lead not only to grinding but also it can cause disordering of the material under treatment, till its amorphization, polymorphous transitions or other mechanochemical transformations. This results in an increase of dissolution rate and solubility, thus, bioavailability increases, too.

In the present investigation we study the effect of mechanical activation on the properties of the effective anti-inflammatory drug piroxicam and the possibility of the mechanochemical synthesis of its complex with  $\beta$ -cyclodextrin.

The mechanical treatment of the samples was carried out in a planetary centrifugal mill AGO-2 (ISSC, Russia) and SPEX8000 mill (CertiPrep, USA). Mechanical activation of the initial piroxicam leads to partial amorphization of the substance. It becomes yellow in course of mechanical treatment; the intensity of colouring increases with increasing treatment time. The change of colour is likely to occur as a result of the rearrangement of piroxicam molecular structure and the appearance of molecules in zwitterionic form. The dissolution rate of mechanically activated samples is substantially higher than that of intact piroxicam.

Mechanical treatment of piroxicam mixed with  $\beta$ -cyclodextrin (1:1, molar ratio) results in the amorphization of the drug. IR and Raman spectroscopic data allow us to conclude that mechanical activation results in the interaction with the formation of intermolecular hydrogen bonds between the reagents. Besides, in Raman spectra we observed the appearance of absorption bands characteristic of the piroxicam -  $\beta$ -cyclodextrin inclusion compound. So, besides the formation of molecular complex, the formation of inclusion compound occurs. Tests for the solubility of mechanically activated mixtures showed that their dissolution rate and the solubility exceed those for both the mechanically activated piroxicam and a physical mixture of piroxicam with  $\beta$ -cyclodextrin.

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## Patent / Brevet

### ONE STEP SYNTHESIS AND CONSOLIDATION OF NANOPHASE MATERIALS

Z.A. Munir, F. Charlot, F. Bernard, E. Gaffet – International patent WO 0112366 (publié le 22.02.2001)

Solid reaction products with a dense nanocrystalline structure are formed from reactant particles with diameters in the nano – scale range by compacting the particles into a green body, then passing an electric current through the body causing Joule heating sufficient to initiate the reaction to form the reaction product while simultaneously applying pressure to the reacting body to densify it to a density approaching the theoretical density of the pure product. Surprisingly, this process results in a reaction product that retains the nanocrystalline structure of the starting materials, despite the fact that a reaction has occurred and the materials have been subjected to highly stringent conditions of electric current, heat and pressure.

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<http://164.195.100.11/netacgi/nph-Parser?Sect1=PTO2&Sect2=HITOFF&p=1&u=/netacgi/search-bool.html&r=1&f=G&l=50&col=AND&d=ft00&sl=gaffet.INZZ.&OS=IN/gaffet&RS=IN/gaffet>

ou encore pour la version brevet d'application

<http://12.espacenet.com/dips/bnsviewer?CY=ep&LG=en&DB=EPD&PN=WO0112366&ID=WO+++0112366A1+I+>

## Périodiques

### [46] CHARACTERISTICS OF MECHANICAL ALLOYING OF ZN-AL-BASED ALLOYS

Zhu YH. Hernandez AP. Lee WB. - Zeitschrift fur Metallkunde. 92(6):578-583, 2001

Three pure elemental powder mixtures of Zn-22%Al-18%Cu, Zn-5%Al-11%Cu, and Zn-27%Al-3%Cu (in wt.%) were mechanically alloyed by steel-ball milling processing. The mechanical alloying characteristics were investigated using X-ray diffraction, scanning electron microscopy, and transmission electron microscopy techniques. It was explored that mechanical alloying started with the formation of phases from pure elemental powders, and this was followed by mechanical milling-induced phase transformation. During mechanical alloying, phases stable at the higher temperatures formed at the near room temperature of milling. Nano-structure Zn-Al-based alloys were produced by mechanical alloying.

### [45] PHASE TRANSFORMATION OF A DUAL PHASE AL-Fe ALLOY PREPARED BY MECHANICAL ALLOYING

Zhou F. Luck R. Lu K. Ruhle M. - Zeitschrift fur Metallkunde. 92(7):675-681, 2001

A metastable Al<sub>90</sub>Fe<sub>10</sub> (at.%) alloy, composed of a supersaturated solid solution of face-centred cubic (fcc) Al(Fe) and an amorphous phase matrix, was prepared by mechanical alloying of a mixture of Al and Fe elemental blends. The thermally induced microstructural evolution in the dual phase alloy was characterized by X-ray diffraction, transmission electron microscopy, differential scanning calorimetry, and magnetothermal analysis. On continuous heating two stages of solid state phase transformation occurred: (i) a polymorphous crystallization of the amorphous phase to a metastable crystalline Al<sub>6</sub>Fe that structurally stabilizes over a temperature range of about 200 K, and (ii) a eutectoid decomposition of the crystalline Al<sub>6</sub>Fe into the equilibrium phases of Al<sub>13</sub>Fe<sub>4</sub> and fcc Al(Fe). Thermodynamic and kinetic analyses of the observed phase transformation processes were given. The formation of the dual phase alloy in the as-milled state and the phase transitions can be illustrated by a hypothetical free energy diagram, implying the dual phase structure facilitates the polymorphous crystallization of Al<sub>6</sub>Fe

### [44] ELABORATION AND STRUCTURE OF NANOSTRUCTURED TIC: A XRD AND HRTEM STUDY

Baviera P. Harel S. Garem H. Grosbras M. - Scripta Materialia. 44(12):2721-2727, 2001

### [44] INFLUENCES OF OXIDE PHASES ON THE COERCIVITY OF MECHANICALLY ALLOYED MULTICOMPONENT FE-BASED AMORPHOUS ALLOYS

Liu YJ. Chang ITH. Lees MR. - Scripta Materialia. 44(12):2729-2734, 2001

### [43] EFFECT OF HYDROGEN ON THE MAGNETIC CHARACTERISTICS OF NANOCRYSTALLINE IRON

Novakova AA. Agladze OV. Kiseleva TY. - Physics of the Solid State. 43(8):1503-1508, 2001.

This paper reports the results of a complex investigation into the properties of nanocrystalline iron prepared through mechanical dispersion in a hydrogen atmosphere. Magnetic measurements reveal changes in the magnetic characteristics of iron samples obtained for different times of milling (i.e., samples with different grain sizes). The structural transformations responsible for these changes are studied by x-ray diffraction, Mossbauer spectroscopy, and thermogravimetry. It is found that incorporation of hydrogen into the boundary region between single-domain particles of consolidated nanocrystalline iron leads to an increase in the coercive force. Magnetic anisotropy induced by strains is observed. It is established that the strain-induced magnetic anisotropy affects the field dependence of the saturation magnetization of nanocrystalline iron

### [42] THE INVARIANT LAWS OF THE AMORPHIZATION PROCESSES BY MECHANICAL ALLOYING - I. EXPERIMENTAL FINDINGS

Delogu F. Schiffini L. Cocco G. - Philosophical Magazine A-Physics of Condensed Matter Defects & Mechanical Properties. 81(8):1917-1937,

Several Ti-, Zr-, Hf- and Nb-based alloys were synthesized using differing milling regimes. Metastable phases, either crystalline or amorphous, develop from the parent elements according to a general sigmoid-shaped behaviour ruled by an interface-controlled kinetic mechanism. The extent of the alloying reactions was related to the operating variables, experimentally determined in the course of the process. Although the transformation rates depended on the milling intensity, that is on the impact energy times the impact frequency, it was found that the reaction yield, defined by the ratio of the transformed fraction to the specific energy dose, is an invariant quantity characteristic of each system. The specific energy



dose defines the mechanical work done on the system per mass unit of the reactants. A rationale for the observed behaviours was provided by the energy needed to reach a given level of the reactant dispersion. Ruling the total extent of the grain boundary area, and the overall kinetics of the alloying process, the work expended in the microstructure refinement was found to be another invariant property of the treated mixtures. The reaction yield is the reference parameter to compare milling trials on an absolute basis, so providing an opportunity towards a quantitative understanding of the mechanical alloying processes

**[41] MODIFICATION OF KAOLINITE SURFACES BY MECHANOCHEMICAL TREATMENT**

Frost RL. Mako E. Kristof J. Horvath E. Klopogge JT. - Langmuir. 17(16):4731-4738, 2001

Kaolinite surfaces were modified by grinding kaolinite/quartz mixtures with mole fractions of 0.25 kaolinite and 0.75 quartz for periods of time up to 4 h. X-ray diffraction shows the loss of intensity of the  $d(0\ 0\ 1)$  spacing with mechanical treatment resulting in the delamination of the kaolinite. Thermogravimetric analyses show the kaolinite surface is significantly modified and surface hydroxyls are replaced with water molecules. Changes in the molecular structure of the surface hydroxyls of the kaolinite/quartz mixtures were followed by infrared spectroscopy. Kaolinite hydroxyls were lost after 2 h of grinding as evidenced by the decrease in intensity of the OH stretching vibrations at 3695 and 3619  $\text{cm}^{-1}$  and the deformation modes at 937 and 915  $\text{cm}^{-1}$ . Changes in the surface structure of the OSiO units were reflected in the SiO stretching and OSiO bending vibrations. The decrease in intensity of the 1056 and 1034  $\text{cm}^{-1}$  bands attributed to kaolinite SiO stretching vibrations were concomitantly matched by the increase in intensity of additional bands at 1113 and 520  $\text{cm}^{-1}$  ascribed to the new mechanically synthesized kaolinite surface. Mechanochemical treatment of the kaolinite results in a new surface structure

**[40] STUDY OF THE PROCESS OF MECHANOCHEMICAL ACTIVATION TO OBTAIN AURIVILLIUS OXIDES WITH N=1**

Ricote J. Pardo L. Castro A. Millan P. - Journal of Solid State Chemistry. 160(1):54-61, 2001

Mechanochemical activation has been successfully used as an alternative method for producing Aurivillius oxides with  $n = 1$ , like  $\text{Bi}_2\text{MoO}_6$ ,  $\text{Bi}_2\text{VO}_5$ , and  $\text{Bi}_2\text{VO}_2$ . The analysis of the mechanoactivated materials by SEM and TEM allows the study of the mechanisms involved in the process of mechanical activation and the occurrence of mechanosynthesis. It is observed that if the amorphization of all the starting oxides is achieved during the process, evidence of mechanosynthesis, i.e., the synthesis of the final product, is found in the resulting particles. The phases obtained either cannot be synthesized by the traditional solidstate reactions or show special characteristics, all of which confirms that the mechanisms of phase formation involved in the mechanical and the thermal activations are different. Further annealing at higher temperatures makes all these structures go back to the phases traditionally obtained by thermal activation.

**[39] INFLUENCE OF THE MILLING CONDITIONS ON THE AMORPHIZATION OF  $\text{Fe}_{82}\text{Nb}_6\text{B}_{12}$  ALLOY**

Caamano Z. Perez G. Zamora LE. Surinach S. Munoz JS. Baro MD. - Journal of Non-Crystalline Solids. 287(1-3):15-19, 2001

$\text{Fe}_{82}\text{Nb}_6\text{B}_{12}$  alloy was synthesized from the elemental powders by a planetary high-energy ball mill, at room temperature, using different milling times and different surfactants. The products were measured by X-ray diffraction, magnetic thermogravimetry, vibrating sample magnetometer, and Mossbauer spectroscopy. Amorphization was observed from the X-ray diffraction on a sample ball milled for about 220 h using 595 rpm and cyclohexane as surfactant. Nevertheless, using the same conditions without surfactant, only the bcc Fe was found. The results are compared with data for rapidly quenched materials.

**[38] STRUCTURAL AND MAGNETIC INVESTIGATION OF MECHANICALLY ALLOYED  $\text{Fe}_{80}\text{Co}_5(\text{Nb}_x\text{Zr}_{1-x})_7\text{B}_8$  POWDERS**

Chiriac H. Moga AE. Urse M. Hison C. - Journal of Non-Crystalline Solids. 287(1-3):50-54, 2001

Experimental results concerning the structural and soft magnetic properties of nanocrystalline  $\text{Fe}_{80}\text{Co}_5(\text{Nb}_x\text{Zr}_{1-x})_7\text{B}_8$  ( $x = 0.3, 0.4$  and  $0.5$ ) powders obtained by high-energy ball milling of elemental powders in argon atmosphere are reported in this work. The initially crystalline diffraction lines corresponding to the unmilled  $\text{Fe}_{80}\text{Co}_5(\text{Nb}_x\text{Zr}_{1-x})_7\text{B}_8$ , ( $x = 0.3, 0.4$  and  $0.5$ ) powders are considerably broadened after ball milling due to the reduction of the crystal sizes and increase of internal strains. The average crystallite sizes, measured by X-ray diffractometry using the Warren-Averbach method, in the final samples obtained after 250 h ball milling were between 7.5 and 11.4 nm. A change in the magnetic properties, measured by vibrating sample magnetometry, of  $\text{Fe}_{80}\text{Co}_5(\text{Nb}_x\text{Zr}_{1-x})_7\text{B}_8$ , ( $x = 0.3, 0.4$  and  $0.5$ ) mechanically alloyed powders is obtained after the thermal treatment of the samples at temperatures between 100 degreesC and 400 degreesC, for 1 h, due to strain relaxation which was measured by X-ray diffractometry

**[37] LOCAL STRUCTURAL ORDERS IN NANOSTRUCTURED FLUORIDE POWDERS**

Guerault H. Bureau B. Silly G. Buzare JY. Greneche JM. - Journal of Non-Crystalline Solids. 287(1-3):65-69, 2001

Nanostructured fluoride powders were prepared by high-energy ball milling under different milling conditions (time and intensity). To investigate the local structural orders, we combined suitable local probe techniques such as Fe-57 Mossbauer spectrometry (MS) and F-19, Ga-69 and Ga-71 nuclear magnetic resonance (NMR) applied to  $\text{FeF}_3$  and  $\text{GaF}_3$  milled samples, respectively. Both isomer shifts and chemical shifts are consistent with the presence of only corner-sharing octahedral units in these systems. After analysis of the different hyperfine magnetic and quadrupolar parameters, the corresponding Mossbauer and nuclear magnetic resonance data were compared to those of crystalline and amorphous phases and then mutually compared. Two types of local structural orders are unambiguously detected and attributed to the presence of crystalline grains and grain



**[36] COMPARISON OF FE-NI-P-SI ALLOYS PREPARED BY BALL MILLING**

Sunol JJ. Clavaguera N. Clavaguera-Mora MT. - Journal of Non-Crystalline Solids. 287(1-3):114-119, 2001

Fe-Ni-P-Si alloys were synthesized from powders in a planetary ball-mill. The microstructure and thermal properties of the milled powders were measured by X-ray diffraction, scanning electron microscopy and differential scanning calorimetry. The diffraction peaks of the individual powders are not detected after the first 32 h of milling time. During milling amorphous and amorphous-like phases are formed. Differential scanning calorimetry results show exothermic reactions for all of the compositions indicating a recovery process as well as crystallization of the amorphous phase. The crystallization products are compared to starting powders. The use of Fe and Ni in the alloy reduces both the energy of formation of the amorphous phase and the time necessary to produce this phase. The incorporation of Si into the Fe-Ni-based alloy favors the formation of a more stable amorphous phase. Moreover, the use of Fe<sub>3</sub>P as starting powder increases the time to form the amorphous phase. The larger the Si content, the greater the thermal stability of the amorphous phase produced during mechanical alloying

**[35] STRUCTURAL AND MAGNETIC PROPERTIES OF MECHANICALLY ALLOYED (Fe<sub>0.5</sub>Mn<sub>0.5</sub>)<sub>(X)</sub>CU<sub>100-X</sub> NANOCRYSTALLINE COMPOUNDS**

Alocen MC. Crespo P. Hernando A. Gonzalez JM. - Journal of Non-Crystalline Solids. 287(1-3):268-271, 2001

We have produced samples with nominal composition (Fe<sub>0.5</sub>Mn<sub>0.5</sub>)<sub>(20)</sub>Cu-80 (at.%) by high-energy ball milling. A structural analysis was undertaken by means of X-ray diffraction (XRD). For milling times around 200 h, the reflections of crystalline Fe cannot be resolved and a single fcc phase is observed, having a lattice parameter larger than fcc-Cu. The grain size is 30 nm. The magnetic properties of the alloy which we observed are: (i) it has coercivities of the order of 25 mT, (ii) susceptibility in a field of 5 T shows that the alloy is polarizable, (iii) low field temperature dependence of the magnetization measured after zero field cooling (ZFC) and field cooling (FC) shows the simultaneous occurrence of two types of magnetic order with differing relaxation times. On the basis of the structural information available, we tentatively identify those types of magnetic order as corresponding to a cluster glass involving both Fe and Mn atoms and to a canonical spin glass.

**[34] MICRO- AND MACROSCOPIC MAGNETIC STUDY OF THE DISORDERING (BALL MILLING) AND POSTERIOR REORDERING (ANNEALING) OF FE-40 AT.% AL**

Amils X. Garitaonandia JS. Nogues J. Surinach S. Plazaola F. Munoz JS. Baro MD. - Journal of Non-Crystalline Solids. 287(1-3):272-276, 2001

The paramagnetic-ferromagnetic transition of Fe-40 at.% Al during ball milling, from 0 to 72 h, (disordering process) and the posterior ferromagnetic-paramagnetic transition with subsequent annealing, from T-ANN = 300 to 975 K, (reordering process) were studied by magnetization and Mossbauer spectroscopy to understand the differences between local and average properties in nanometric systems. The overall properties observed from both techniques are similar despite the atomic scale data of Mossbauer spectroscopy and macroscopic properties measured by magnetization, respectively. The differences between both types of results, e.g., 10-20% larger paramagnetic contribution or 10-20% smaller normalized hyperfine field - magnetization observed from Mossbauer spectroscopy, are a consequence of the microscopic-macroscopic length scales of each technique and the limitations of the data analysis

**[33] MECHANICALLY ALLOYED LOW-NICKEL AUSTENITE FE-NI PHASE: EVIDENCE OF SINGLE-PHASE PARAMAGNETIC STATE**

Kaloshkin SD. Tcherdyntsev VV. Baldokhin YV. Tomilin IA. Shelekhov EV.- Journal of Non-Crystalline Solids. 287(1-3):329-333,

Fe<sub>100-x</sub>Ni<sub>x</sub> alloys were obtained by a mechanical alloying technique (MA) from elemental metals. The alloys consist of: single body-centered cubic phase (bcc) at nickel concentrations less than or equal to 22 at.%, single face-centered cubic phase (Fcc) - at  $x > 28$  at.% and two of these phases - at 22 less than or equal to  $x$  less than or equal to 28 at.%. Annealing results in formation of single fcc phase structure in the samples with  $x$  greater than or equal to 22 at.%. According to the Mossbauer spectrometry data these annealed alloys with 22-28 at.% Ni were not ferromagnetic at room temperature. Cooling austenitic samples in liquid nitrogen as well as mechanical deformation stimulated austenite-martensite transformation accompanied by the appearance of ferromagnetism

**[32] PHASE TRANSFORMATIONS IN CO-B-SI ALLOYS INDUCED BY HIGH-ENERGY BALL MILLING**

Pekala M. Jachimowicz M. Fadeeva VI. Matyja H. - Journal of Non-Crystalline Solids. 287(1-3):360-365, 2001

X-ray diffraction analysis, differential scanning calorimetry and magnetization measurements were used to determine the structural changes of the Co<sub>78</sub>B<sub>11</sub>Si<sub>11</sub> alloys prepared by a ball milling of amorphous, crystallized ribbons and a mixture of elemental crystalline powders in vibratory mill. For all starting materials the high-energy ball milling of Co<sub>78</sub>B<sub>11</sub>Si<sub>11</sub> alloy produces a crystalline structure with nanometer sized crystals. The average crystallite size is about 5 nm. Three series of Co<sub>78</sub>B<sub>11</sub>Si<sub>11</sub> alloys are the ferromagnetic materials. Milling of amorphous alloys causes an increase of the room temperature magnetic moment from 0.90 to 1.08  $\mu$ <sub>B</sub>. A similar tendency is observed for alloys produced by milling of the initially crystallized ribbons for which the magnetic moment increases from 0.73  $\mu$ <sub>B</sub> at  $t = 0$  to 1.17  $\mu$ <sub>B</sub> after 250 h. Somewhat different dependence is found for alloys milled from powders since magnetization of the alloy subjected to longer milling is reduced by 10% due to structural disorder introduced during a formation of the crystalline Co(Si,B) phase with nanometer sized crystals

**[31] MAGNETIC AND STRUCTURAL STUDIES OF BALL MILLED FE<sub>78</sub>B<sub>13</sub>SI<sub>9</sub>**

Pekala M. Jachimowicz M. Fadeeva VI. Matyja H. Grabias A. - Journal of Non-Crystalline Solids. 287(1-3):380-384, 2001

We report on high-energy ball milling of Fe<sub>76</sub>B<sub>13</sub>Si<sub>9</sub> alloy prepared from amorphous and crystallized ribbons as starting materials as well as from a mixture of pure elemental powders. The X-ray diffraction (XRD), differential scanning



calorimetry (DSC), magnetization and Mossbauer measurements were carried out. High-energy ball milling processes form nanocrystalline Fe-based solid solution for all starting materials investigated. The average grain size was in the range 8-16 nm. By mechanical crystallization of amorphous Fe<sub>78</sub>B<sub>13</sub>Si<sub>9</sub> alloy we obtain two phase mixture of supersaturated alpha - Fe(Si, B) solid solution. The volume fraction of amorphous phase depends on the milling time. In the case of milling crystalline materials (mixture of crystalline powders or crystallized ribbon), continuous refinement of the microstructure was observed. Dissolution of Si and B atoms in Fe lattice during mechanical alloying of elemental powders occurred simultaneously with crystallite size reduction. The grain size reduction to the nanometer range is accompanied by an increase in atomic-level strain. Decreasing of grain size and increasing of the atomic-level strain lead to the decomposition of the Fe<sub>2</sub>B compound during the milling of the crystallized ribbon. Boron atoms dissolve in the Fe crystalline lattice forming supersaturated alpha -Fe(Si, B) solid solution. Similar effect was observed during prolonged milling of mechanically crystallized ribbon. All the alloys studied are ferromagnetic with Curie temperatures exceeding 850 K independent of a starting materials. The magnetic moments are reduced with increasing milling time. A multiphase composition is also confirmed by Mossbauer spectroscopy

**[30] PREPARATION OF PMN POWDERS AND CERAMICS VIA A HIGH-ENERGY BALL MILLING PROCESS**

Kong LB. Ma J. Zhu W. Tan OK. - Journal of Materials Science Letters. 20(13):1241-1243, 2001.

**[29] AMORPHOUS AND NANOCRYSTALLINE (FE<sub>0.5</sub>CO<sub>0.5</sub>)(60)CU<sub>2</sub>V<sub>8</sub>B<sub>30</sub> PREPARED BY MECHANICAL ALLOYING**

Ji YL. Wang GH. Li F. Wang GQ. Zhao JW. Zhang SY. - Journal of Materials Science Letters. 20(13):1267-1269, 2001.

**[28] INFLUENCE OF MECHANICAL ACTIVATION EFFECT ON THE Y<sub>2</sub>SI<sub>2</sub>O<sub>7</sub> FORMATION**

Tzvetkov G. Minkova N. - Journal of Materials Science Letters. 20(14):1273-1275, 2001.

**[27] MECHANOCHEMICAL EFFECT ON MG-ALLOYS BY IMPEDANCE MEASUREMENTS**

Bonora PL. Andrei M. Eliezer A. Gutman EM. - Journal of Materials Science Letters. 20(14):1349-1351, 2001.

**[26] MECHANICALLY ALLOYED CU-FE STUDIED BY MOSSBAUER SPECTROSCOPY**

Principi G. Spataru T. Gupta R. Enzo S. Kuncser V. Filoti G. - Journal of Alloys & Compounds. 326(1-2):188-192, 2001  
Recent studies of mechanically alloyed Fe-Cu powder mixtures have suggested differences in the local magnetic environment of iron atoms. For a more accurate definition of this point, ball-milled Cu<sub>70</sub>Fe<sub>30</sub> and Cu<sub>50</sub>Fe<sub>50</sub> alloys were investigated by Mossbauer spectroscopy in the, temperature range 4.2-300 K. The low temperature Mossbauer spectra exhibit a broad magnetic pattern, typical of a defect structural configuration. The magnetic splitting strongly decreases with increasing temperature, especially in the case of Cu<sub>70</sub>Fe<sub>30</sub> alloy. But even for this composition there is, at room temperature, an unresolved magnetic pattern. Applying a magnetic field of 3 T, parallel to gamma rays, at 4.2 K a rotation of all magnetic moments along the external field is observed. The samples behave as an alloy with continuously distributed local fields

**[25] NANOPHASE IRON OXIDES BY BALL-MILL GRINDING AND THEIR MOSSBAUER CHARACTERIZATION**

Bid S. Banerjee A. Kumar S. Pradhan SK. De UY. Banerjee D. - Journal of Alloys & Compounds. 326(1-2):292-297, 2001

Ball-mill grinding of ferric oxide, Fe<sub>2</sub>O<sub>3</sub>. to obtain nanophase samples has been undertaken for different duration with repeated X-ray diffraction monitoring of nanophase formation. Particle size and strain have been calculated from XRD patterns, for different periods of ballmilling at 300 rpm. Mossbauer spectra of as-supplied or bulk iron oxides and these finely ballmilled samples have been compared looking for the signature of superparamagnetism possible in the nanophase samples

**[24] THERMAL AND MORPHOLOGICAL STUDIES ON ETHYLENE-VINYL ACETATE COPOLYMER-POLYANILINE BLENDS**

Jeevananda T. Siddaramaiah. - Thermochimica Acta. 376(1):51-61, 2001

A series of ethylene-vinyl acetate copolymer-polyaniline (EVA-PAn) blends with different weight ratios of PAn were obtained by mechanical blending using plasticorder. Thermogravimetric analysis (TGA) studies of the blends were performed in order to establish the mode of their thermal degradation. The TGA thermograms showed that the thermal degradation of EVA-PAn blends was found to proceed in three steps except in the case of EVA-PAn (90/10) blend system. Degradation kinetic parameter was obtained for each stage of thermal degradation of blends, using Broido and Coats-Redfern methods. The activation energy (E) of the blends for the thermal degradation process lie in the range of 3.3-95.6 kJ/mol and of 9.6-135.0 kJ/mol for Broido and Coats-Redfern methods, respectively. The surface morphology of the EVA-PAn blends was analyzed by scanning electron microscopy (SEM) before and after thermal treatment.

**[23] COERCIVITY AND SQUARENESS ENHANCEMENT IN BALL-MILLED HARD MAGNETIC-ANTIFERROMAGNETIC COMPOSITES**

Sort J. Nogues J. Surinach S. Munoz JS. Baro MD. Chappel E. Dupont F. Chouteau G. - Applied Physics Letters. 79(8):1142-1144,

The room-temperature coercivity, H-C, and squareness, M-R/M-S (remanence/saturation magnetizations), of permanent magnet, SmCo<sub>5</sub> powders have been enhanced by ball milling with antiferromagnetic NiO (with Neel temperature, T-N=590 K). This enhancement is observed in the as-milled state. However, when the milling of SmCo<sub>5</sub> is carried out with an antiferromagnet with T-N below room temperature (e.g., for CoO, T-N=290 K), the coercivity enhancement is only observed at low temperatures after field cooling through T-N. The ferromagnetic-antiferromagnetic exchange coupling induced either by local heating during milling (SmCo<sub>5</sub>+NiO) or field cooling (SmCo<sub>5</sub>+CoO) is shown to be the origin of the H-C increase.

**[22] FORMATION OF ZR-NI-BASED AMORPHOUS ALLOYS WITH WIDE SUPERCOOLED LIQUID REGION BY MECHANICAL ALLOYING**

Liu L. Zhang J. - Materials Research Bulletin. 36(11):2073-2082,



The amorphous  $Zr_{64}Ni_{36}$ ,  $Zr_{60}Ni_{25}Al_{15}$ ,  $Zr_{65}Ni_{10}Cu_{17.5}Al_{17.5}$ , and  $Zr_{63}Ni_{10}Cu_{17.5}Al_{17.5}C_2$  alloys were successfully synthesized by mechanical alloying of pure element powders. The structural evaluation of powder mixtures in the process of milling was monitored by X-ray diffraction and scanning electron microscopy. The thermal stability of the amorphous alloys obtained and the compositional effects on the glass forming ability were analyzed by differential scanning calorimetry. It was found that, except for  $Zr_{64}Ni_{36}$ , other three amorphous alloys exhibit a distinct glass transition and wide supercooled liquid region ranging from 63 to 82 degreesC. The amorphous  $Zr_{60}Ni_{25}Al_{15}$  alloy exhibits the highest glass transition and crystallization temperatures, while the amorphous  $Zr_{63}Ni_{10}Cu_{17.5}Al_{17.5}C_2$  phase shows the largest supercooled liquid region. The results demonstrate that addition of appropriate amounts of C extends the supercooled liquid region of Zr-Ni-based amorphous alloys. The effect of the C addition on the glass-forming ability of Zr-Ni-based systems is discussed.

**[21] PIEZOELECTRIC CERAMICS BASED ON  $Bi_3TiNbO_9$  FROM MECHANOCHEMICALLY ACTIVATED PRECURSORS**

Moure A. Pardo L. Alemany C. Millan P. Castro A. - Journal of the European Ceramic Society. 21(10-11):1399-1402, 2001.

Ceramics based on the Aurivillius type structure compound  $Bi_3TiNbO_9$  were processed by natural sintering and hot pressing of amorphous precursors obtained by mechanochemical activation of oxides and carbonates mixtures. Synthesis, grain growth and sintering take place in a single thermal treatment at moderate temperatures in comparison with ceramics processed from crystalline precursors. The influence of the processing parameters on the ceramic texture and microstructure at mesoscopic scale were studied by XRD and quantitative optical microscopy. It was possible to obtain both isotropic and textured ceramics. The occurrence of abnormal grain growth was observed under some conditions. An ample electrical characterisation of the ceramics was carried out comprising dielectric, ferroelectric and piezoelectric properties. The influence of the microstructure on the properties and the interest of the materials as high temperature piezoelectrics are discussed

**[20] MICROCHARACTERISATION OF GRAIN-ORIENTED CERAMICS BASED ON  $Bi_3TiNbO_9$  OBTAINED FROM MECHANOCHEMICALLY ACTIVATED PRECURSORS**

Ricote J. Pardo L. Moure A. Castro A. Millan P. Chateigner D. - Journal of the European Ceramic Society. 21(10-11):1403-1407, 2001.

Hot pressing was applied to a novel powder, synthesised by the mechanochemical activation of starting oxides, in order to obtain dense ceramics of  $Bi_3TiNbO_9$  for use as piezoelectric material at high temperatures. Since these compositions belong to the family of layered perovskites, hot pressing produces a preferential orientation of the grains. An assessment of the degree of orientation achieved was carried out by quantitative texture analysis using experimental X-ray pole figures. Although texture could be considered as the most influential factor on the final properties, other microstructural features were studied by transmission electron microscopy including grain boundaries and ferroelectric domains. The results of the microcharacterisation of these ceramics are discussed in order to understand the process involved in the development of preferential orientation in these ceramics

**[19] EFFECT OF MILLING PROCESS ON CORE-SHELL MICROSTRUCTURE AND ELECTRICAL PROPERTIES FOR  $BaTiO_3$ -BASED NI-MLCC**

Mizuno Y. Hagiwara T. Chazono H. Kishi H. - Journal of the European Ceramic Society. 21(10-11):1649-1652, 2001.

The effect of the process parameter in the milling process on the microstructural evolution and the electrical properties of multilayer ceramic capacitor (MLCC) samples were investigated in the  $BaTiO_3$  (BT)- $Ho_2O_3$ -MgO system. The microstructure for MLCC samples fired at 1320 degreesC was dependent on the degree of damage for BT given by the milling process, judging from the field emission scanning electron microscopy observation and differential scanning calorimetry measurement (DSC). The mean grain size (D-50) determined from the chemically etched samples decreased as the damage increased. The endothermic peak of DSC profile at around 125 degreesC was broadened and the peak area decreased as the damage increased. Furthermore, the electrical properties were dependent on the degree of damage. The dielectric constant for MLCC samples decreased and the peak of dielectric constant at around room temperature shifted to a higher temperature as the damage increased. It was found that the MLCC sample showed the small leakage current and long mean lifetime as the degree of damage increased.

**[18] MECHANOCHEMICAL SYNTHESIS OF  $BaTiO_3$ ,  $Bi_0.5Na_0.5TiO_3$  AND  $Ba_2NaNb_5O_{15}$  DIELECTRIC CERAMICS**

van Hal HAM. Groen WA. Maassen S. Keur WC. - Journal of the European Ceramic Society. 21(10-11):1689-1692, 2001.

In the last years, mechanochemical alloying has been proven to be an important technology for the synthesis of intermetallic compounds. This technology has recently been used as a new route for the synthesis of inorganic compounds. The use of mechanochemical synthesis opens possibilities for the synthesis of complex systems at low temperatures. In this paper we discuss the preparation of the powders  $BaTiO_3$ ,  $Bi_0.5Na_0.5TiO_3$  and  $Ba_2NaNb_5O_{15}$  by mechanochemical synthesis. Phase formation is studied by X-ray powder diffraction. Since partly amorphous powders are obtained the crystallisation behaviour is further investigated by high temperature X-ray powder diffraction. Ceramic pellets have been sintered starting from as-milled powders as well as pre-fired powders. Microstructure and dielectric properties are characterised

**[17] THE INFLUENCE OF MECHANICAL ACTIVATION ON ZINC STANNATE SPINEL FORMATION**

Nikolic N. Sreckovic T. Ristic MM. - Journal of the European Ceramic Society. 21(10-11):2071-2074, 2001.

Mechanical activation of inorganic materials leads to specific changes of their chemical and physical properties. Grinding, as one way of mechanical activation, is a widely used method for obtaining highly dispersed systems, and it could be performed in various types of mills (planetary, centrifugal, vibro-mill, etc.). The development of advanced materials is, therefore,



dependent not only on the investigated material, but on characteristics of a device as well. Polycrystalline zinc stannate spinel,  $Zn_2SnO_4$ , is a material used for combustible gases and humidity detection, photo electrochemical applications, coatings, etc. The subject of this work is the influence of mechanical activation on solid state chemical reaction, e.g. the formation of porous zinc stannate ceramics during different thermal treatments of compacts obtained from ZnO and SnO<sub>2</sub> powder mixtures mechanically activated in a high energy vibro-mill. X-ray diffraction analysis, scanning electron microscopy and non-isothermal dilatometric measurements were performed in order to investigate spinel formation

**[16] DISPERSION AND SLIP CASTING OF HYDROXYAPATITE**

Rao RR. Kannan TS. - Journal of the American Ceramic Society. 84(8):1710-1716, 2001

The dispersibility in deionized water of hydroxyapatite (HA) synthesized by a high-temperature (1000 degreesC) solid-state reaction between tricalcium phosphate and calcium hydroxide was investigated as a function of the pH of the medium and the quantity of two dispersing agents (A = inorganic, B = organic) added to the slips. Although pH modification had a negligible effect on dispersibility, both of the dispersing agents produced a good dispersion at considerably higher concentrations (>2 wt% of HA). At optimum amounts (2-4 wt%) of the dispersing agents, the slips showed near-Newtonian flow behavior up to 45 wt% solids loading and non-Newtonian behavior at > 50 wt%. By the optimal addition of dispersing agents and conditioning by ball milling, 60-67 wt% (32-39 vol%) solids-loaded HA slips could be cast into plaster molds to produce 50%-58% dense green bodies, which, in turn, sintered to 90%-94% density in the temperature range 1300 degrees - 1400 degreesC. The sintered HA exhibited a three-point flexural strength of 40-60 MPa and a homogeneous microstructure, with interspersed microporosities

**[15] PRODUCTION OF ANTIBIOTIC NANOPARTICLES USING SUPERCRITICAL CO<sub>2</sub> AS ANTISOLVENT WITH ENHANCED MASS TRANSFER**

Chattopadhyay P. Gupta RB. - Industrial & Engineering Chemistry Research. 40(16):3530-3539, 2001

Drug delivery systems improve the therapeutic efficacy and safety of drugs by delivering them at a controlled rate depending on the body requirements and the site of action. These systems aid in reducing the amount of drug required, the number of doses, side effects, and bioinactivation. Currently, delivery systems for drug targeting and controlled release are being developed using drug nanoparticles. Several techniques, such as spray drying and milling, have been used in the past for the manufacture of drug nanoparticles, but these methods have several disadvantages. Supercritical fluid technologies such as RESS and SAS do provide novel methods for particle formation, but in most cases, they still cannot produce particles in the nanometer range (< 300 nm) necessary for drug targeting and controlled release. In this work, we propose a technique that can produce drug particles in the nanometer range with a narrow size distribution. This new technique is a modification of the currently existing SAS technique and involves the use of a vibrating surface that atomizes the jet into microdroplets. The ultrasonic field generated by the vibrating surface also enhances mass transfer through increased mixings. The new technique is demonstrated for the production of tetracycline nanoparticles as small as 125 nm in size with a narrow size distribution. Particle sizes are easily controlled using this technique by changing the vibrational intensity of the vibrating surface

**[14] MECHANOCHEMICAL MODEL TO PREDICT STRESS CORROSION CRACK GROWTH OF STAINLESS STEEL IN HIGH TEMPERATURE WATER**

Saito K. Kuniya J. - Corrosion Science. 43(9):1751-1766, 2001

This paper presents a predictive methodology for SCC crack growth using a mechanochemical model based on a slip formation/dissolution mechanism. The mechanochemical model consists of the combined kinetics of the plastic deformation process as a mechanical factor and the slip dissolution-repassivation process as an environmental factor at a crack tip. The predictive equation of SCC crack growth rate for type 304 SS in water at 288 degreesC is formulated as a function of stress intensity factor, material conditions (degree of sensitization, K-ISCC, strain hardening coefficient) and water chemistry (water conductivity, corrosion potential). The theoretical predictions according to the mechanochemical model are quantitatively in good agreement with many experimental observations of the effect on SCC crack growth for type 304 SS in 288 degreesC water

**[13] ON THE REACTION SEQUENCE OF WC-CO FORMATION USING AN INTEGRATED MECHANICAL AND THERMAL ACTIVATION PROCESS**

Ban-ZG; Shaw-LL - ACTA-MATERIALIA. SEP 3 2001; 49 (15) : 2933-2939

A systematic study on the reaction sequence of WC-Co composite formation by annealing high energy ball milled WO<sub>3</sub>, CoO and graphite powder mixtures in a hydrogen atmosphere has been conducted. X-ray diffraction has been used as the main tool to analyze the phase transformation of the powder mixture during processing. It was observed that WO<sub>3</sub> is reduced to W phase by passing through the intermediate W<sub>2</sub>O<sub>5</sub> and WO<sub>2</sub> phases and the subsequent carburization sequence appears as W --> Co<sub>6</sub>W<sub>6</sub>C --> Co<sub>3</sub>W<sub>3</sub>C --> W<sub>2</sub>C --> WC. The intermediate Co<sub>3</sub>W has been found in the reduction stage, which can be subsequently carburized at higher temperatures

**[12] MECHANOCHEMICAL SYNTHESIS OF NANOCRYSTALLINE HYDROXYAPATITE FROM CAO AND CAHPO<sub>4</sub>**

Yeong-KCB; Wang-J; Ng-SC - BIOMATERIALS-. OCT 2001; 22 (20) : 2705-2712.

Ceramic hydroxyapatite phase was triggered to occur by high-energy mechanical activation of a dry powder mixture of calcium oxide (CaO) and anhydrous calcium hydrogen phosphate (CaHPO<sub>4</sub>). A single-phase hydroxyapatite of high crystallinity was realised by > 20h of mechanical activation without further thermal treatment at high temperatures. The resulting hydroxyapatite powder exhibits an average particle size of similar to 25 nm and a specific surface area of 76.06 m<sup>2</sup>/g, as measured by multi-point BET technique. It was sintered to a density of 98.20% theoretical density at 1200 C for 2 h.

**[11] STRUCTURE AND MAGNETIC PROPERTIES OF POWDERS PREPARED BY MECHANICALLY ALLOYING 50FE+25AL+25SI MIXTURES**



Fadeeva-VI; Sviridov-IA; Nikitin-SA; Ovtsenkova-YA - INORGANIC-MATERIALS. AUG 2001; 37 (8) : 790-796  
A 50Fe + 25Al + 25Si powder mixture was mechanically alloyed in a high-energy ball mill, and the products of the solid-state reactions were characterized by x-ray diffraction and magnetic measurements. The results show that the process involves the formation of a metastable bcc Fe < Al,Si > solid solution, which decomposes into the ordered phases FeAl<sub>1-x</sub>Si<sub>x</sub> (B2 structure) and FeSi (B20) upon heating to 700 degreesC or long-term milling. The observed effect of milling on the magnetic properties of the powders indicates that the proportion of the ferromagnetic component in the alloy decreases with increasing milling time as a result of the ordering of the solid solution and the formation of the B2 and B20 paramagnetic phases.

**[10] DIRECT CRYSTAL TO GLASS TRANSFORMATION OF TREHALOSE INDUCED BY BALL MILLING**

Willart-JF; De-Gusseme-A; Hemon-S; Odou-G; Danede-F; Descamps-M - SOLID-STATE-COMMUNICATIONS. 2001; 119 (8-9) : 501-505.

Structural and thermodynamic changes in the organic molecular crystal of trehalose upon high energy ball milling have been studied. The investigations have been performed by X-ray diffraction and by differential scanning calorimetry. The results show that mechanical milling induces a direct transformation from crystal to glass. It is underlined that glassy amorphous trehalose can also be produced by two other independent routes: the thermal quench of the liquid state and the dehydration of the dihydrate form of trehalose. This makes trehalose a promising molecular crystal for the fundamental study of the solid state amorphization processes themselves

**[9] THE EFFECT OF HIGH ENERGY BALL MILLING ON THE CRYSTAL STRUCTURE OF GdNi<sub>5</sub>**

Stubicar-M; Blazina-Z; Tonejc-A; Stubicar-N; Krumes-D SO: PHYSICA-B. SEP 2001; 304 (1-4) : 304-308

X-ray powder diffraction was used to determine the effect of, dry, in air performed high energy ball milling, on the intermetallic compound GdNi<sub>5</sub>. It was found that the crystal structure of GdNi<sub>5</sub> is not stable. At the early stage of milling (up to after 10 h of milling) the gadolinium component oxidises causing thus the decomposition of GdNi<sub>5</sub> into monoclinic Gd<sub>2</sub>O<sub>3</sub> and metallic nickel. Both, the crystallite (grain) size and the particle size of powder decrease during the early stage of milling. At the later stage of milling (up to 50 h) the nickel phase from the mixture of Gd<sub>2</sub>O<sub>3</sub> and nanocrystalline nickel oxidises into nanocrystalline NiO. Therefore, the final product after 150 h of milling of GdNi<sub>5</sub> is a mixture of oxides of the constituent metals. i.e., amorphous Gd<sub>2</sub>O<sub>3</sub> and nanocrystalline NiO. Traces of contamination by alpha -SiO<sub>2</sub> have been observed in the milled powder, being more pronounced as the milling process proceeds. This is ascribed to the wear effect of agate milling assembly.

**[8] STRUCTURE AND MECHANICAL BEHAVIOR OF AN ALUMINUM ALLOY AMG6 AFTER SEVERE PLASTIC DEFORMATION AND ANNEALING: 2. MECHANICAL PROPERTIES**

Markushev-MV; Murashkin-MY - PHYSICS-OF-METALS-AND-METALLOGRAPHY. JUL 2001; 92 (1) : 84-91

Room-temperature mechanical behavior of a commercial AMg6 alloy with submicrocrystalline and microcrystalline structures resulting from severe plastic deformation by equal-channel angular pressing and subsequent annealing was considered. The serrated flow and the static-strength characteristics including cracking resistance were considered as a function of the structural state of the alloy.

**[7] THE INFLUENCE OF MECHANICAL ACTIVATION ON ZINC STANNATE SPINEL FORMATION**

Nikolic-N; Sreckovic-T; Ristic-MM - JOURNAL-OF-THE-EUROPEAN-CERAMIC-SOCIETY. 2001; 21 (10-11) : 2071-2074.

Mechanical activation of inorganic materials leads to specific changes of their chemical and physical properties. Grinding, as one way of mechanical activation, is a widely used method for obtaining highly dispersed systems, and it could be performed in various types of mills (planetary, centrifugal, vibro-mill, etc.). The development of advanced materials is, therefore, dependent not only on the investigated material, but on characteristics of a device as well. Polycrystalline zinc stannate spinel, Zn<sub>2</sub>SnO<sub>4</sub>, is a material used for combustible gases and humidity detection, photo electrochemical applications, coatings, etc. The subject of this work is the influence of mechanical activation on solid state chemical reaction, e.g. the formation of porous zinc stannate ceramics during different thermal treatments of compacts obtained from ZnO and SnO<sub>2</sub> powder mixtures mechanically activated in a high energy vibro-mill. X-ray diffraction analysis, scanning electron microscopy and non-isothermal dilatometric measurements were performed in order to investigate spinel formation.

**[6] MECHANOCHEMICAL SYNTHESIS OF BaTiO<sub>3</sub>, Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> AND Ba<sub>2</sub>NaNb<sub>5</sub>O<sub>15</sub> DIELECTRIC CERAMICS**

van-Hal-HAM; Groen-WA; Maassen-S; Keur-WC - JOURNAL-OF-THE-EUROPEAN-CERAMIC-SOCIETY. 2001; 21 (10-11) : 1689-1692.

In the last years, mechanochemical alloying has been proven to be an important technology for the synthesis of intermetallic compounds. This technology has recently been used as a new route for the synthesis of inorganic compounds. The use of mechanochemical synthesis opens possibilities for the synthesis of complex systems at low temperatures. In this paper we discuss the preparation of the powders BaTiO<sub>3</sub>, Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> and Ba<sub>2</sub>NaNb<sub>5</sub>O<sub>15</sub> by mechanochemical synthesis. Phase formation is studied by X-ray powder diffraction. Since partly amorphous powders are obtained the crystallisation behaviour is further investigated by high temperature X-ray powder diffraction. Ceramic pellets have been sintered starting from as-milled powders as well as prefired powders. Microstructure and dielectric properties are characterised

**[5] DISPERSION AND SLIP CASTING OF HYDROXYAPATITE**

Rao-RR; Kannan-TS - JOURNAL-OF-THE-AMERICAN-CERAMIC-SOCIETY. AUG 2001; 84 (8) : 1710-1716

The dispersibility in deionized water of hydroxyapatite (HA) synthesized by a high-temperature (1000 degreesC) solid-state reaction between tricalcium phosphate and calcium hydroxide was investigated as a function of the pH of the medium and the quantity of two dispersing agents (A = inorganic, B = organic) added to the slips. Although pH modification had a negligible effect on dispersibility, both of the dispersing agents produced a good dispersion at considerably higher concentrations (>2 wt% of HA). At optimum amounts (2-4 wt%) of the dispersing agents, the slips showed near-Newtonian flow behavior up to 45 wt% solids loading and non-Newtonian behavior at > 50 wt%. By the optimal addition of dispersing agents and conditioning by ball milling, 60-67 wt% (32-39 vol%) solids-loaded HA slips could be cast into plaster molds to produce 50%-58% dense green bodies, which, in turn, sintered to 90%-94% density in the temperature range 1300 degrees - 1400 degreesC. The sintered HA exhibited a three-point flexural strength of 40-60 MPa and a homogeneous microstructure, with interspersed microporosities



**[4] COERCIVITY AND SQUARENESS ENHANCEMENT IN BALL-MILLED HARD MAGNETIC-ANTIFERROMAGNETIC COMPOSITES**

Sort-J; Nogues-J; Surinach-S; Munoz-JS; Baro-MD; Chappel-E; Dupont-F; Chouteau-G - APPLIED-PHYSICS-LETTERS. AUG 20 2001; 79 (8) : 1142-1144

The room-temperature coercivity, H-C, and squareness, M-R/M-S (remanence/saturation magnetizations), of permanent magnet, SmCo5 powders have been enhanced by ball milling with antiferromagnetic NiO (with Neel temperature, T-N=590 K). This enhancement is observed in the as-milled state. However, when the milling of SmCo5 is carried out with an antiferromagnet with T-N below room temperature (e.g., for CoO, T-N=290 K), the coercivity enhancement is only observed at low temperatures after field cooling through T-N. The ferromagnetic-antiferromagnetic exchange coupling induced either by local heating during milling (SmCo5+NiO) or field cooling (SmCo5+CoO) is shown to be the origin of the H-C increase

**[3] FORMATION OF ZR-NI-BASED AMORPHOUS ALLOYS WITH WIDE SUPERCOOLED LIQUID REGION BY MECHANICAL ALLOYING**

Liu-L; Zhang-J - MATERIALS-RESEARCH-BULLETIN. SEP 15 2001; 36 (11) : 2073-2082

The amorphous Zr64Ni36, Zr60Ni25Al15, Zr65Ni10Cu17.5Al7.5, and Zr63Ni10Cu17.5Al7.5C2 alloys were successfully synthesized by mechanical alloying of pure element powders. The structural evaluation of powder mixtures in the process of milling was monitored by X-ray diffraction and scanning electron microscopy. The thermal stability of the amorphous alloys obtained and the compositional effects on the glass forming ability were analyzed by differential scanning calorimetry. It was found that, except for Zr64Ni36, other three amorphous alloys exhibit a distinct glass transition and wide supercooled liquid region ranging from 63 to 82 degreesC. The amorphous Zr60Ni25Al15 alloy exhibits the highest glass transition and crystallization temperatures, while the amorphous Zr63Ni10Cu17.5Al7.5C2 phase shows the largest supercooled liquid region. The results demonstrate that addition of appropriate amounts of C extends the supercooled liquid region of Zr-Ni-based amorphous alloys. The effect of the C addition on the glass-forming ability of Zr-Ni-based systems is discussed

**[2] MECHANOCHEMICAL SYNTHESIS OF BaTiO3, Bi0.5Na0.5TiO3 AND Ba2NaNb5O15 DIELECTRIC CERAMICS**

van-Hal-HAM; Groen-WA; Maassen-S; Keur-WC - JOURNAL-OF-THE-EUROPEAN-CERAMIC-SOCIETY. 2001; 21 (10-11) : 1689-1692

In the last years, mechanochemical alloying has been proven to be an important technology for the synthesis of intermetallic compounds. This technology has recently been used as a new route for the synthesis of inorganic compounds. The use of mechanochemical synthesis opens possibilities for the synthesis of complex systems at low temperatures. In this paper we discuss the preparation of the powders BaTiO3, Bi0.5Na0.5TiO3 and Ba2NaNb5O15 by mechanochemical synthesis. Phase formation is studied by X-ray powder diffraction. Since partly amorphous powders are obtained the crystallisation behaviour is further investigated by high temperature X-ray powder diffraction. Ceramic pellets have been sintered starting from as-milled powders as well as prefired powders. Microstructure and dielectric properties are characterised.

**[1] SYNTHESIS OF ULTRAFINE MANGANESE-FERRITE POWDERS BY MECHANOCHEMICAL PROCESSING**

M Muroi, J Amighian, R Street, PG McCormick - MAGNETIC AND SUPERCONDUCTING MATERIALS, (MSM - 99), VOLS A AND B, 2000, pp 1091-1098 - 1ST REGIONAL CONFERENCE ON MAGNETIC AND SUPERCONDUCTING MATERIALS (MSM-99); TEHRAN, IRAN. SEPTEMBER 27-30, 1999

Ultrafine MnFe2O4 powders have been synthesised via the displacement reaction  $2\text{FeCl}(3) + 4\text{MnO} \rightarrow \text{MnFe}_2\text{O}_4 + 3\text{MnCl}(2)$  activated by high-energy ball milling. Single-phase MnFe2O4 powders having crystallite sizes ranging between 9.5 and 40 nm have been obtained after removing the by-product (MnCl2) and unreacted (FeCl3 and MnO) phases from the as-milled or annealed powders by washing and magnetic separation. Magnetic measurements show that the spontaneous magnetisation decreases with crystallite size; that the coercivity increases with decreasing temperature; and that below about 20 K, the temperature dependence of coercivity becomes very strong and the hysteresis loop becomes asymmetric with an enhanced remanence and coercivity in the upper branch when the sample is cooled in the maximum field. These observations are discussed in terms of a model in which it is assumed that each crystallite consists of a ferrimagnetic core surrounded by a spin-glass shell and the spins in the core and shell are coupled through exchange interactions at the interface.



## Press release

### DRY DISPERSING UNIT FOR "analysette 22" – LASER PARTICLE SIZER

In many sectors of industry, knowledge of the particle size distribution of pulverised material or suspensions is a vital aspect of quality control. Measurement of this characteristic also plays a noteworthy role in production monitoring (e.g., of crushing plants).

*FRITSCH*, with their vast experience in the particle-sizing field, is now presenting a new dispersing unit that measures particle size distributions of dry solid samples in a free jet.

**This new dry dispersing unit utilises mechanical and pneumatic forces to prepare agglomerates. The supply of sample is metered by a high-tech, amplitude-controlled vibratory feeder. Dispersion is achieved with cooling fins in a two-phase annular gap nozzle. Waves forming aerodynamically at the nozzle outlet ensure a high flow rate.**

This new development enables *FRITSCH* to dramatically expand the possible applications of the well-known, tried-and-tested "analysette 22" Laser Particle Sizer family and to offer a state-of-the-art particle size measuring instrument for any special application and any budget:

#### **Laser Particle Sizer "analysette 22" COMFORT**

**for fast, automatic measurement of particle size distributions of suspensions, emulsions and dry powders.**

Measuring range:

**for suspensions + emulsions: 0.1 - 1250 microns**

**for dry powders: 0.8 - 1250 microns**

#### **Laser Particle Sizer "analysette 22" ECONOMY**

The budget-priced "ECONOMY" VERSION is available for routine measurements in the range of **0.1 to 600 microns**. Designed for fast, automatic determination of particle size distributions of any **solids in suspension and emulsions**.

#### **Laser-Particle-Sizer "analysette 22" COMPACT**

Due to the Laser Particle Sizer "analysette 22" COMPACT from *FRITSCH*, users whose budgets previously prohibited them from doing so are now able to enter the era of high-tech laser technology. With the COMPACT model it is possible to quickly, economically and efficiently measure particle sizes in the **0.3 to 300 µm** range in **suspensions, emulsions and solids**.

**FRITSCH thus satisfies the demands of industry and research to permit utilisation of state-of-the-art laser technology at a remarkable cost-to-performance ratio.**

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