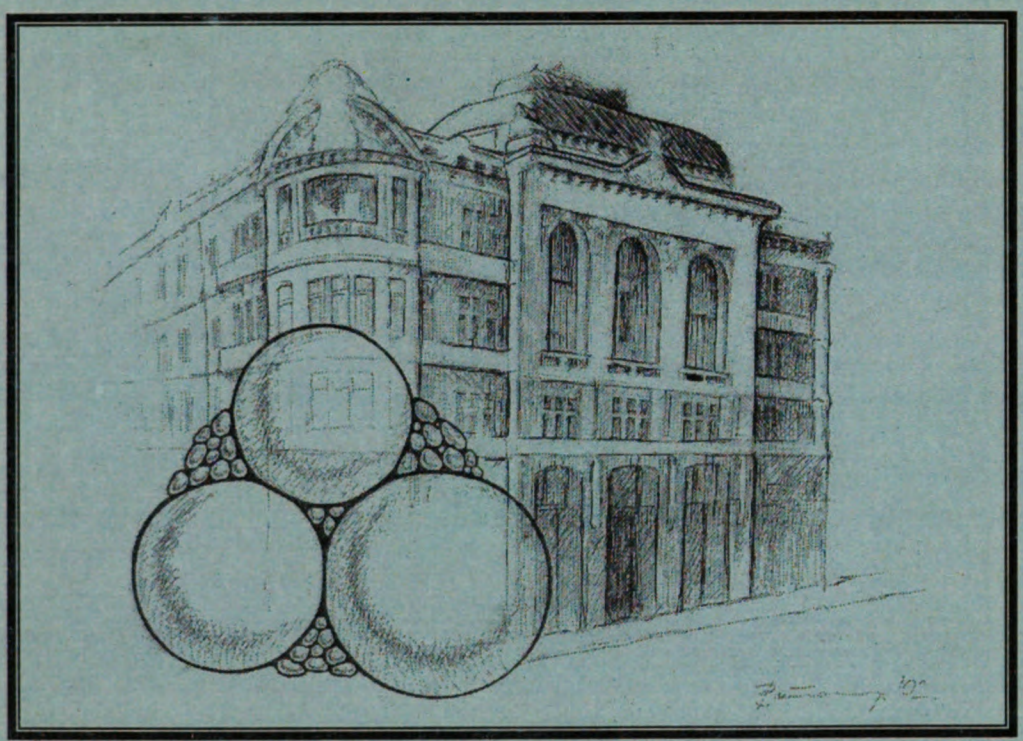
SCIENCE OF SINTERING IN THE XXI CENTURY



Edited by
Maria Vesna Nikolic and Natasa Nikolic

SCIENCE OF SINTERING IN THE XXI CENTURY

Book of Abstracts

X World Round Table Conference on Sintering
3 - 6 September 2002
Belgrade, Yugoslavia

SERBIAN ACADEMY OF SCIENCES AND ARTS
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INTERNATIONAL INSTITUTE FOR THE SCIENCE OF SINTERING
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INSTITUTE OF TECHNICAL SCIENCES OF SASA

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Book of Abstracts
X World Round Table Conference on Sintering

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PREFACE

This book contains abstracts of papers presented at the X World Round Table Conference on Sintering (WRTCS) held from 3-6 September 2002 at the Serbian Academy of Sciences and Arts (SASA) in Belgrade. As a rule these Conferences are organized by SASA and the International Institute for the Science of Sintering (IISS) and held quaternary in Yugoslavia and gather prominent scientists from all over the world to discuss current problems in the science and technology of sintering.

The tenth WRTCS scientific papers deals with the fundamental issues regarding science of sintering, nanoparticles and nanotechnology, powder synthesis and processing, sintered advanced materials, properties of sintered materials and evolution of the microstructure.

Editors

FUNDAMENTALS

SOME NEW ASPECTS IN THE ANALYSIS OF A LIQUID-PHASE SINTERING

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The processes of mass transport during reaction liquid-phase sintering of multicomponent systems are reviewed. Special emphasis is focused on the behavior of dopants, which enable changes of the solubility of components in the solid phase and in the melt. The systems of choice, which provide formation of intermetallic compounds on the surface of a high melting phase, are four-component systems with two high melting components of different thermodynamic affinity with respect to the melt. The effect of diffusion and non-diffusion transport through the liquid phase on kinetics of densification and grain growth of the high melting phase as well as on the formation of a rigid skeleton and alloying kinetics in a high melting subsystem during isothermal sintering is analyzed. For all these processes the role of a scaling factor is estimated. Genesis of the microstructure of a sintered material is considered from the standpoint of the influence of its geometrical parameters on physical and mechanical properties.

DEFINITION OF THE TERM "SINTERING"

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The definition of the term "sintering" as of the process which results in densification of a powder body at high temperatures under the action of capillary forces is valid only for the special case, when a single-phase or one-component powder body is exposed to sintering. Such a definition is not general as it is not suitable for the case of sintering power bodies pressed from mixtures, which can suffer not shrinkage, but an essential growth in volume during sintering owing to the formation of alloys and compounds. Because diffusion processes of the

formation of alloys and compounds during sintering bring in directly a contribution to mass transport causing a change of mixtures in volume, they are an organic part of the sintering phenomenon. Moreover, the driving force for the process of alloy and compound formation surpasses by one or two orders of magnitude the driving force for the densification process under the action of surface tension. Therefore, it is the mode of the alloy and compound formation, which defines the sign and value of the volume change of the mixture during sintering. Because the change of mixed compacts in volume and in their properties during sintering occurs owing to the formation of alloys and compounds as well as under the influence of surface tension forces of interparticle pores, it is possible to define the term "sintering" as thermal treatment of a powder body, which changes its dimensions and physical-mechanical properties as a result of diffusion flow of the material under the action of alloy formation and capillary forces.

3-D VISUALIZATION OF THE LIQUID BRIDGE DURING LIQUID PHASE SINTERING

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The rearrangement process assumes that if there is good wetting between the liquid and solid phase, solid particles will rearrange themselves under the action of surface tension forces, producing more stable packing. Therefore it is very interesting to investigate how the solid particles rearrange. In that sense, it is very important to make an analysis of the resulting capillary forces as the driving forces of liquid phase sintering. This can be the first step for a study of the rearrangement processes in an array of solid particles that are connected by liquid bridges. This paper outlines a computer-based method for 3-D visualization of a liquid bridge between two spherical particles, which can be used for the study of interparticle forces during liquid phase sintering.

THE DEFECT MODES IN VIBRATIONAL SPECTRA OF HIGHLY DISORDERED SILICA GEL DURING THE SINTERING PROCESS: A COMPUTER SIMULATION STUDY

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Synthesis and sintering conditions can cause many structural defects in the silica gel structure. Small rings (three and four membered) form in a shape, which is not a minimum energy configuration. In Raman spectra defect modes of irregular rings move to higher frequencies. In the infrared spectra defect modes are not visible. However, irregularity of a small ring causes the appearance of defect modes in the infrared spectra too. During the sintering process these rings become regular. We used a semi empirical method - MNDOd (modified neglect of diatomic overlap) for calculations of vibrational spectra of models containing the ring structure, which corresponds to the gel structure during the sintering process. The calculated vibrational spectra are in agreement with Raman spectra of series of sintered samples. Using simulation results we explained the appearance of defect modes in infrared spectra of the same sintered series.

ELECTRON ASPECT OF STRUCTURE FORMATION IN TRANSITION METAL ALLOYS

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Application of an auxilary concept of "technological properties" frequently carries out closing of parts in the Materials Science triad "technology - structure-properties". The theoretical unsoundness of such a method is obvious: the concept of "property", by definition, is characterized as a reversible response of the structure to external or internal influences, and technology is characterized only as

an irreversible response. Such a method becomes unproductive or even harmful, especially, on a nanolevel, and in practice research reaches a deadlock. For example, when the real task of non-equilibrium relaxation-atomic consolidation of particles is substituted by the analysis of diffusion movement under action of surface forces in the case of sintering, the opportunity of describing the technology of clusters or fullerens is lost. Peculiarities of structure formation connected with specific electron-atomic effects - "nestings" on a Fermi surface (electronic system instability), soft phonon modes (lattice system instability), creation of charge- or spin-density waves, variable – valence states etc. are not analyzable as a result of such an approach. The consecutive methodology of Materials Science assumes system consideration of a fundamental triad in the scheme based on the first principles of the quantum-statistical theory, and a set of global constants. The system-creating factor is the external influence or a generalized force in such a scheme. The technological features of a system at any structural level are described in terms of deeper levels. The proposed system consideration is an elaboration of our previous work, and is demonstrated on examples of titanium and zirconium alloys with their electron, crystal and mezoscopical structure, which has already been thoroughly investigated.

EVALUATION OF MECHANICAL PROPERTIES OF ALUMINA VIA THE PROPERTY-MICROSTRUCTURE DIAGRAM

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Morphological changes of microstructure during sintering and their effect on mechanical properties were analyzed using defect-free alumina made by High-Speed Centrifugal Compaction Process (HCP). Morphological change during sintering, expressed by a combination of density and grain size, constitutes a unique trajectory on the grain-size/relative-density map. The combination is essentially irrespective of sintering conditions. However, the trajectories shift their locations when a different starting powder or different sintering techniques (microwave sintering) are used. The effect of density (or porosity) and grain size

on hardness and strength are empirically derived using Knudsen's equations. The equations provide contour lines, which represent microstructures having the same hardness or strength on the grain-size/relative-density map and form property-microstructure diagrams. The diagrams can be used to determine the optimum sintering conditions as well as to estimate maximums of attainable hardness and strength.

HYDROXYAPATITE/POLYLACTIDE COMPOSITE BIOMATERIALS FOR HARD TISSUE RECONSTRUCTION

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This paper gives a review on the synthesis, design and implementation of hydroxyapatite/poly-l-lactide (HAp/PLLA) composite biomaterials. This kind of composite can be used for the reconstruction of hard bone tissue. Polymer resorption, after potential implementation, classifies this group of composites into smart biomaterials that enable formation and proliferation of the new connecting tissue. Designing the HAp and PLLA properties enables the dynamics of this process. There are different ways of obtaining these kinds of composites, from classic mixing of HAp and PLLA, polymerization of the mix of the l-lactide monomer and HAp, to complex processing by forging and hot pressing. The production method influences the structure and properties, which has a direct consequence on the behaviour of these composite biomaterials during bone tissue reconstruction. Until now, HAp/PLLA blocks with mechanical properties similar to natural bone tissue were obtained only by the procedures of forging and hot pressing. During *in vitro* and *in vivo* research performed by different researchers and authors it was established that implants of HAp/PLLA do not show signs of significant inflammatory response. After implantation, PLLA bioresorption was established with simultaneous appearance of a new fibrous tissue. Fibers that connect the HAp granules and particles are of collagen nature. All previous results emphasize the possibility of using HAp/PLLA composite biomaterials for the reconstruction of large bone damage, of any kind or origin, which would enable a better quality of life and a longer life of every potential patient.

A NEW MODEL FOR THE CALCULATION OF SWELLING EFFECTS DURING TRANSIENT LIQUID PHASE SINTERING

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Reactive sintering in the presence of a transient liquid phase is an interesting route for the preparation of many intermetallic materials. However, considerable problems result from severe volume changes during the sintering process due to swelling processes. Such processes prevent a full and homogeneous densification of the material by pressureless sintering. The aim of this paper is to propose a new model, which allows an exact calculation of the maximum values for swelling during reactive sintering of Ti-Al-elemental powder mixtures. The validity of the calculated values is proven by several experiments. Furthermore it is shown that the results can be used to produce intermetallic materials with defined porosity that can be used for several applications as high temperature filters.

THERMODYNAMICS NATURE OF HUND'S CORRELATION OF d AND f ELEMENTS

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The well known electronic theory of the sintering process is based on the configuration model of a material. At the same time the macroscopic theory of the sintering process is based a thermodynamic analyses of different models of diffusion and different defects. On the basis of these two facts in this paper we introduce one approach, which enables the definition of a unique thermodynamics electronic theory by computing statistically stable configurations d^5 and f^7 by a semi classic analyses of systems with five and seven states. We used the law of equipartition of energy and the law of equipartition of particles as the starting point of this model.

MODEL OF THERMODIFFUSION DURING THE SINTERING PROCESS

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By analyzing infinite lattices, the diffusion of atoms along characteristic directions and planes might be considered, during the isothermal sintering process, by separating subsystems with a constant number of the particles. In that sense, the diffusion process might be considered as overtaking the thermal equilibrium determined by the maximal subsystem entropies. It leads to changes of the particle number in accessible states. This way, an original model of thermodiffusion was obtained which enables a relativelly simple analysis of some stages of the sintering process. Using the obtained results, with a unique view, we were able to consider different ways during the sintering process of ceramic powders.

MODELING OF THE SiC WETTING PROCESS USING MORPHOLOGICAL ANALYSIS

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Processing of metal matrix composites is very sensitive to the wetting characteristics of the reinforcement phase, which is in many cases a ceramic phase. In this paper SiC substrate was used as a ceramic phase for investigating wetting characteristics of the Al-Mg alloy for making MMC composites with an Al-based matrix. Molten Al-Mg alloy with a Mg content up to 7 mass% was held at 700, 800 and 900°C, in which SiC substrates were immersed for different times (up to 900 seconds). After each 30 seconds substrates were taken out of the melt, cooled down

and analysed by SEM (Philips SEM 515). Morphological on-line analysis of formed structures on the substrate was performed using the Osaria image processing program. Classification of obtained structures included the form factor, structure area and fractal dimensions. A model of the metal matrix formation mechanism was then established using a morphological analysis of these surface forms.

FEATURES ON AN ELECTRONIC STRUCTURE AND PHYSICAL PROPERTIES OF REFRACTORIES ON THE BASIS OF CONFIGURATION-UNSTABLE ELEMENTS

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In the light of the fundamental "technology – structure – properties" triad the laws of formation of basic and exited conditions in materials based on Ce, Sm, Eu, Yb are considered, electronic subshells which show instability to d→f or f→d electronic transitions. The existing electronic models for the description of abnormal behaviour of physical properties of such connections based on the account of interactions between located and grouped electrons are compared. The parameters determining abnormal behaviour are allocated and the opportunities of their directed change by technological means are shown.

EFFECT OF BARIUM AND STRONTIUM ADDITION ON THE STRUCTURE AND PROPERTIES OF PZT OBTAINED BY THE POLYMERIC PRECURSOR METHOD

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Lead zirconate titanate powder, with Zr/Ti ratio of 50/50 was prepared by the Pechini method after adding up to 10.0 mol.% of Ba^{+2} and Sr^{+2} ions. A tetragonal phase is favored by the increase of barium and strontium concentration in the PZT crystal lattice. The ratio c/a for the tetragonal phase increases with the content of Ba^{+2} and Sr^{+2}. The addition of Ba^{+2} promotes densification of PZT ceramics while the Sr^{+2} addition decreases. Increasing strontium additive concentration leads to an increase of both, K_p and d_{33}. Increasing the barium additive concentration leads to a decrease of both, K_p and d_{33}. This is due to the formation of $BaTiO_3$ and ZrO_2 rich second phases at the grain boundaries.

SINTERING KINETICS OF SnO_2 DOPED WITH MnO_2

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Sintering kinetics of SnO_2 doped with different amounts of MnO_2 (0.2 - 1 mol.%) was investigated. Non-isothermal sintering was monitored by a dilatometer for temperatures up to 1350°C, with a heating rate of 2.5°C/min, in argon atmosphere. The sintering mechanism was determined at the initial stage using the model of Bannister and Woolfrey. The activation energy of sintering was calculated by Dorn's method. The sintering process started with characteristic viscose flow rearrangement of grains in all investigated compositions. The activation energy of sintering showed a minimum value of 600 $kJmol^{-1}$ for 0.34 % MnO_2.

EFFECT OF THE STRAIN DEGREE DURING ANNEALING ON THE KINETICS AND THERMODYNAMICS OF THE CRYSTALLIZATION PROCESS OF THE $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ AMORPHOUS ALLOY

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The differential scanning calorimetry method was used for investigating the kinetics and thermodynamics of the crystallization process of $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ alloy samples previously isothermally annealed at 380, 400 and 420°C for 30 min. Samples were exposed to strain degrees of 130, 300 and 475 MPa during isothermal annealing. The thermograms obtained for all samples show that the crystallization process occurs exothermically in three stages. The peak temperature of the first exothermic maximum moves to higher temperatures with strain degrees increase. The stress influence on the temperatures of other peaks is insignificant. The obtained thermal parameters point out that enthalpy of the crystallization process depends on the strain degree and has the lowest value for all three peaks at the 300 MPa strain degree. The kinetic parameters of the crystallization process were determined for samples exposed to the 475 MPa strain degree during isothermal annealing at 420°C.

THE KINETICS OF SINTERING OF REAL DISPERSE MATERIALS

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In real technological conditions, the process of sintering is very complex, and in order for this process to occur, a simultaneous action of a whole range of

elementary processes is necessary. In accordance with the aforementioned, and starting from the model for sintering of dispersive materials, while taking into consideration the theoretical principles of transportation of materials in porous systems, this paper analyzes, first of all, the current state of this field. On the basis of the above mentioned, and particularly the physical essence of the processes responsible for the process of sintering, an original model for describing the kinetics of the sintering process has been developed. The appropriate simulation, starting from the parameters, which define the real system, has been performed. Besides, the original software for analysis the kinetics of sintering of real materials has been developed.

INFLUENCE OF MECHANICAL ACTIVATION ON SINTERING KINETICS $CaO\text{-}TiO_2$ OF THE SYSTEM

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Ceramic materials have been in use in many different areas of human life for a very long time. Important domains in ceramic materials are those materials that are applied in electronics. Our research is focused on calcium-titanate ($CaTiO_3$). The most common way of obtaining this material is by using the process of sintering. During mechanical activation inorganic materials are ground and their grain size is reduced. The crystal structure submits to distortion and also changes, which in some systems leads to a chemical reaction and formation of a new compound. We will explaining mechanical the influence of mechanical activation on sintering kinetics in the $CaO\text{-}TiO_2$ system. Mechanical activation of initial powders is performed by grinding in a high-energy vibro-mill for 60 minutes. Calcination was performed for 2 hours at 900°C after which samples were pressed and then sintered at temperatures of 1000, 1100, 1200 and 1300°C for 180 minutes. X-ray diffraction is used for observing the evolution of the calcium-titanate phase

during research. DTA measurements of initial powders were performed. Regarding the equations related to this phenomenon and Gropianov's theory, we explained the influence of mechanical activation on sintering kinetics. We noticed a temperature drop and time reduction needed for $CaTiO_3$ sintering when the duration of mechanical activation is longer.

CRYSTALLIZATION BEHAVIOUR OF $PbO-B_2O_3-ZnO$ GLASS CONTAINING Li_2O

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Oxide glasses with a high content of lead are the most important group of low melting glasses for industrial application. Besides classical use as glazes and enamels during recent years the area of application of these glasses has been expanded to the fields of electronics and microelectronics (solder or sealing glasses, thick film capacitors and resistors etc.). Besides a low melting temperature the glasses should have a thermal expansion coefficient compatible with other materials in the system, chemical stability, high electric resistance, thermal stability preventing crystallization and other specific properties. The bases for the development of these glasses are the $PbO-B_2O_3-SiO_2$, $PbO-B_2O_3-ZnO$ and $ZnO-B_2O_3-SiO_2$ systems. The main properties of the base glassy systems usually changed by addition of a small amount of alkali metal cations or other cations such as Ti, Ba, Cd, Ge, Ta, Cu etc. The goal of this work is investigation of the effect of LiO_2 on the crystallization behavior of low melting solder $PbO-B_2O_3-ZnO$ glass. The investigation was performed using differential thermal analysis (DTA) and X-ray powder diffraction (XRPD) methods. The results showed that addition of a small amount of Li_2O in the base glass changes the sequence of crystallization and the phase composition of the crystalline phase formed during crystallization. The base glass crystallizes at a higher temperature with $PbO{\cdot}2ZnO{\cdot}B_2O_3$ as the main crystallizing phase. During crystallization of the glasses containing Li_2O $Li_2O{\cdot}2ZnO{\cdot}3B_2O_3$ and $4Li_2O{\cdot}4ZnO{\cdot}3B_2O_3$ phase were detected.

CRYSTALLIZATION OF CALCIUM-ALUMINOPHOSPHATE INVERT GLASS

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Inclusion of modifier into glassy P_2O_5 results in depolymerization of the tetrahedral [PO_4] network. Increase in the content if the cation modifier is accompanied by significant modification of its structure, from a cross-linked network of the tetrahedra via the polymer-like chains of the tetrahedra to invert glasses based on small pyro- and orthophosphate anions, depending on the [O]\[P] ratio. However, when alkali and alkaline earth phosphate glasses are exposed to aqueous solutions, phosphate anions are rapidly hydrated and dissolve intact into the solution. Glass durability can be improved significantly by the addition of Al_2O_3 which cross-links neighboring phosphate anions with more hydration-resistant Al-O-P bonds. For these reasons the [O]\[P] ratio tends to increase at [O]\[P] > 3.5 because stable phosphate glasses exhibit a tendency towards faster structure arrangement – crystallization. The chemical composition of Ca-phosphate glasses, similar to the composition of teeth and bones, make them ideal candidates for biomedical applications. In general, calcium polyphosphate glasses undergo surface crystallization. For this reason, kinetics and mechanism of their crystallization are always in the focus of interest. In this paper the crystallization of a calcium-aluminophosphate invert glass containing 5 wt.% TiO_2 was studied. The investigations were performed under non-isothermal conditions. The results show complex crystallization behavior of this glass. In the crystallization temperature range T > 900°C, β-calcium pyrophosphate (β-$Ca_2P_2O_7$) is formed. The following kinetic parameters of this process are determined: the activation energy of crystal growth E_{a1} = 373 ± 19 kJ/mol and Avrami parameter n = 1.25 ± 0.2. In the temperature interval T > 900°C β-calcium pyrophosphate (β-$Ca_2P_2O_7$) and titanium phosphate (TiP_2O_7) are formed. The kinetic parameters of crystallization of TiP_2O_7 are: the activation energy of crystal growth E_{a2} = 260 ± 9 kJ/mol and Avrami parameter n = 3.2 ± 0.4.

AN ANALYSIS OF EXISTING CONCEPTS OF PHENOMENOLOGICAL LAWS OF SINTERING KINETICS AND POSSIBILITIES FOR DEFINING AN IMPROVED MODEL

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Investigations of sintering on idealized models, such as the ones defined by Frenkel, Pines and Kuczynski, give basic information on the kinetics and mechanism of the sintering process. As they cannot be directly applied to real systems, they have been the basis for the development of phenomenological theories for defining the sintering process of real systems. Equations given by Ristic-Jovanovic, Geguzin and Ivensen have been applied in the greatest number of cases in literature. This paper contains a comparative analysis of experimental data for Fe and NaF powders using these three different phenomenological approaches. A modification of the Ristic-Jovanovic equation, with a reduced number of parameters has also been applied. A new model that observes movement of atoms and vacancies as Fermi excitation of a solid state lattice is also described.

KINETICS OF SOLID STATE PROCESSES IN THE ALUMINUM SLAG–SODIUM HYDROXIDE SYSTEM

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The development of technologies of advanced materials is investigated by fundamental and applied research in the field of solid state processes. In accordance with this, processes occurring during the aluminum-sodium hydroxide reaction have been investigated. The slag contains a mixture of aluminum oxide and non-precious metals. This mixture also contains finely distributed liquid metal.

Isothermal investigations of the solid state reactions in this system have shown that the process of decomposition at the phase distribution interface limits the rate. Temperature has a more significant influence than the duration of the final process. The soaking rate of aluminum oxide is limited by diffusion through the solid state formation layer. A complex analysis of all results obtained has established principles of the "technology-structure-properties" relationship.

INFLUENCE OF THE Al_2O_3 CONTENT ON THE GROWTH KINETICS OF INTER-PARTICLE CONTACTS DURING SINTERING OF THE Cu/Al_2O_3 SYSTEM

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The growth of inter-particle contacts in the science of sintering has mostly been investigated during heating of loose powders. It was based on theoretical principles of sintering of models. In this paper, we have investigated the growth of these contacts between copper particles in the Cu/Al_2O_3 system. This way, in dependence on the Al_2O_3 content, contact growth between copper particles is slowed down. This enabled more precise following of the growth of the basic material. An analysis of experimentally obtained data was performed under the assumption that the same process mechanism determined both local particle deformation in the contact area and macroscopic volume deformation of the porous body as a whole.

OBTAINING, STRUCTURE AND PROPERTIES OF BIONERT CERAMIC FOAM

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Solids having a foamlike structure are used in numerous applications, including filters, diffusers, catalyst supports, thermal insulation, lightweight structural laminates, biomaterials etc. The understanding of the relation between processing, macrostructure and properties will be beneficial to the production of these materials. The properties of solid foam depend on the cellular geometry and the properties of the material comprising the solid phase. Open cell foams consist of a reticulated network of interconnected struts. This structure can be considered to be a mutually interconnected composite material, as the solid and void phases are both three-dimensionally connected in space. TiO_2, Al_2O_3 and Al_2O_3-TiO_2-SiO_2 bioinert materials are of particular interest. These materials can be used in dense and porous form. As creators of porous structure PVA, H_2O_2, polyurethane foam, and carbon fibres were used. The obtained porosity was 55-82 %. The variation of E-modulus, shear modulus and Poisson's ratio with porosity can be shown in the form of E-functions. In dependence on the porosity creators, the pore size was 200-1000 μm, E-modulus was 8-18 GPa and bending strength 10-20 MPa. These porous bioinert materials can find a potential application in medicine.

MECHANICAL AND THERMAL-EXPANSION CHARACTERISTICS OF THE $Ca_{10}(PO_4)_6(OH)_2$–$Ca_3(PO_4)_2$ COMPOSITE

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The aim of this work was obtaining of the $Ca_{10}(PO_4)_6(OH)_2$–$Ca_3(PO_4)_2$ composite, its consolidation and determination of the thermal-expansion characteristics, in order to define its thermal stability. A $Ca_{10}(PO_4)_6(OH)_2$–$Ca_3(PO_4)_2$ composite was prepared by mixing the component powders. Three different systems of composites with various percentages of $Ca_3(PO_4)_2$ from 25 – 75 mass% were obtained. The systems were isostatically pressed under the pressure of 400 MPa and sintered in air, at the temperature of 1200°C, for one hour. E-modulus, Poisson's number and the Shear modulus of the consolidated systems were determined by ultra-sound method. Thermal expansion characteristics and thermal stability were determined using the dilatometric method. Correlation between mechanical and thermal-expansion characteristics was performed applying several model equations. It was shown that Kerner's equation

$$\alpha_c = \frac{[\alpha_i f K_i /(3K_i + 4G_m)] + [\alpha_m(1-f) K_m/ (3K_m + 4G_m)]}{[f K_i /(3K_i + 4G_m)] + [(1-f) K_m/ (3K_m + 4G_m)]}$$

gives the best correlation between mechanical and thermal-expansion characteristics.

THERMAL-EXPANSION AND MECHANICAL PROPERTIES OF THE $Ca_{10}(PO_4)_6(OH)_2$–TiO_2 COMPOSITE

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Hydroxyapatite (HAp: $Ca_{10}(PO_4)_6(OH)_2$) is a particularly attractive material for human tissue implantation. HAp has a similar chemical composition and crystal structure to apatite in the human skelet system and is therefore suitable for bone substitution and reconstruction. The intrinsic poor mechanical properties of HAp material can lead to instability and unsatisfactory duration of the implant in the presence of body fluids and local loading. Therefore HAp needs to be strengthened. The addition of titanium dioxide in the HAp matrix can enhance the mechanical properties of the obtained composite. The aim of this investigation was

obtaining of a HAp–TiO_2 composite and defining a correlation between mechanical and thermal-expansion properties. The composite was obtained by dry mixing of the starting powders: HAp (company Merck) and TiO_2 (produced by the hydrolysis method). The consolidation of the composite was realized by issostatic pressing under the pressure of 400 MPa and sintering at 1230°C/2h, with a heating rate of 5°/min. The composite with 15 % TiO_2 content shows thermal stability of the system and improved mechanical properties.

CROSS-LINKING OF AN INJECTABLE POLYDIMETHYLSILOXANE/HYDROXYAPATITE BIOCOMPOSITE CEMENT

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Cements, which may play different roles when applied in an organism, have been used for fixing various prostheses in orthopedic surgery. Calcium-hydroxyapatite (HAp) based cements belong to a special group. New demands for better quality and application of cements arose with the development of surgery, especially in cases of filling up the hollows and repair of hard and soft tissues when surgical intervention is to be avoided. One of the demands is to inject a solution into hollows or defects, which then controllably solidifies meeting previously determined functional, biocompatible and bioactive requirements. For that reason, injectable calcium-phosphate cements have been developed for orthopedic surgery applications. An injectable gas-permeable polydimethylsiloxane/hydroxyapatite (PDMS/HAp) composite cement, using linear PDMS and HAp (particles of about 100 nm in size) of different mass fractions, was synthesized. Differential scanning calorimetry (DSC) was used to study the cross-linking process and the influence of HAp on temperature and duration of the PDMS/HAp system cross-linking. Based on DSC research, a decrease in temperature of cross-linking PDMS with supplements of HAp up to 20 mass% was established. Total heat of cross-linking

also notes maximum value (approximately 30 J/g) for the part of HAp of 20 mass%. Increase in heating rate (from 5 to 40 K/min) conditions an increase of temperature with simultaneous decrease in total heat of cross-linking process. The optimal part of the precursor that enables cross-linking, is approximately 10 mass% while its further increase or decrease leads to the increase in temperature and decrease of the total heat of the cross-linking process.

PREPARATION OF POROUS HYDROXYAPATITE BY UNIDIRECTIONAL FREEZING OF GEL

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The design and synthesis of porous materials and/or fibres is a current challenge in solid state chemistry. For many applications, the precise control of pore dimensions is the limiting factor. For the preparation of Ca-P colloidal suspension (sol-gel) solutions of a calcium nitrate tetrahydrate and an ammonium dihydrogen orthophosphate were mixed to produce the desired colloidal suspension. The resultant colloidal suspension (sol-gel) is inspected for any abnormal precipitation or agglomeration. If any abnormal precipitation or agglomeration has occurred, the solution must be discarded and preparation commenced again. The resulting Ca-P colloidal suspension is continuously stirred at moderate speed for approximately 24 hours and then directionally frozen by lowering a plastic cilinder into a liquid nitrogen bath. In this case, products with various morphological characteristics, from ribbed flakes to polygonally cross-secioned fibres are obtained. In general, formation of various morphological forms depends on the electrolyte concentration, gel strength and unidirectional freezing rate.

"BUILDING SICKNESS": THE INFLUENCE OF A PHOSPHOGYPSUM PARTION WALL ON THE TOTAL RADIOACTIVITY OF BUILDING

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The study of phosphogypsum use in gypsum fiberboard partition walls has proved functional qualities thereof, speaking also of potential substitution of pure gypsum [1]. This is what makes substantial savings in natural materials possible, as wel as reduction of harmful effects of phosphogypsum waste deposits on the environment. Analyses performed in this work have shown a significant presence of radionuclides in phosphogypsum [2]. Gammaspectrometric measurements of radioactivity have determined substantial radioactivity of phosphogypsum. Using the Maximum tolerated level values that are legally accepted, as well as equations to calculate indexes of tolerated radionuclide presence:

$$\text{Index for interiors} = \frac{^{226}\text{Ra (Bq/kg)}}{200} + \frac{^{232}\text{Th (Bq/kg)}}{300} + \frac{^{40}\text{K(Bq/kg)}}{3000} + \frac{V_{\text{interiors}}\,\text{(Bq/kg)}}{4000} \leq 1$$

$$\text{Index for exteriors} = \frac{^{226}\text{Ra (Bq/kg)}}{400} + \frac{^{232}\text{Th (Bq/kg)}}{300} + \frac{^{40}\text{K(Bq/kg)}}{5000} + \frac{V_{\text{exteriors}}\,\text{(Bq/kg)}}{4000} \leq 1$$

$$\text{Index for roads} = \frac{^{226}\text{Ra (Bq/kg)}}{700} + \frac{^{232}\text{Th (Bq/kg)}}{500} + \frac{^{40}\text{K(Bq/kg)}}{8000} + \frac{V_{\text{for roads}}\,\text{(Bq/kg)}}{2000} \leq 1$$

an index of 2.23 has been determined for interiors, that of 1.13 for exteriors, i.e. 0.64 in case of roads. On the basis of the Maximum tolerated level of radioactive building materials contamination (<1), the use of phosphogypsum in interiors is forbiden, it is allowed (≈1) in exteriors and roads. Tests of heavy metal components in phosphogypsum have proved presence thereof, however in

quantities potentially producing consequences if present in closed spaces. That causality is conditioned by the phosphogypsum quantity, as well as by the area of space partitioned.

1. M.B. Rajkovic, D. Simovic, G.T. Vladisavljevic, Experiences in the Chemical Gypsum–Phosphogypsum Preparation From the Triad "Synthesis–Structure–Properties" Viewpoint", in "*Advanced Science and Technology of Sintering*", Eds. Biljana D. Stojanovic, Valery V. Skorokohd and Maria Vesna Nikolic, Kluwer Academic/Plenum Publishers, New York, 1999, p. 323–328.
2. M.B. Rajkovic, K. Karljikovic–Rajic, G.T. Vladisavljevic, I.S. Ciric, Investigation of Radionuclides in Phosphogypsum, Measurement Techniques, **42** (3) (1999) 299–305.

NANOPARTICLES AND NANOTECHNOLOGY

SIZE EFFECTS IN NANOSTRUCTURED MATERIALS SCIENCE

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In recent 10-15 years, there has been increased interest in nanostructured materials (NMs). Size effects in properties of NMs are of great importance from both fundamental considerations and modern practice. As a whole in materials science the effect of the grain size on the material properties is a long-explored problem. It is common knowledge that there are many relationships in this field such as the Hall–Petch equation, the Coble, and the Nabarro-Herring ones and so on. However, there are at least four principal features of size effects in NMs. The first is the increase of the role of interfacial defects (grain boundaries, triples, etc.). The second is that properties of these interfacial defects in a nanointerval may be not the same as in conventional materials. The third is the overlapping of the grain size with characteristic physical length (L_{PHYS}). The fourth is the possibility of a quantum effect revealation. All these things may result in the presence of some specific points in the size dependencies and the availability of unmonotonous change in the properties determined by the grain size decreasing. In this context it seems of interest to consider the upper and lower limits of the NM grain size. By NMs, the materials are commonly meant in which the size of the grains or phases composing their structure does not exceed 100 nm at least in one direction. This upper limit is very arbitrary and its value is dictated by convenience considerations rather than physical ones. It is clear also that the values of L_{PHYS} (e.g., the Frank–Read loop size for dislocation slip, the free path of carriers for transport properties, the domain features for magnetic characteristics, etc.) would differ for different properties and different metals, alloys, and compounds. Because of this, the value of L_{PHYS} can not be the upper limit of grain size for NMs. It is worth noting that the lower limit of the NM grain size can be about 1 nm. There are not so many observations for NMs with such small crystallites. To our knowledge, such small crystallites (<1 - 2 nm) have been observed only in nanostructured films. Accumulation of knowledge of such cluster-consolidated solids will provide additional insight into the nature of the nanocrystalline state. In addition, the chances that the quantum size effects can be revealed in these objects seem to be likely.

SINTERING OF TIN OXIDE NANOPOWDERS

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The sintering process of nanometric undoped SnO_2 powder (25-120 nm) was studied. No macroscopic shrinkage was observed during the sintering process. Surface diffusion is the dominant mechanism in the temperature range of 500-1300°C. For temperatures higher than 1300°C, high weight loss was measured, suggesting evaporation-condensation as the dominant mass-transport mechanism. TG and mass spectroscopy studies showed that the surface contamination of the SnO_2 particles by chemical species like H_2O, OH^- and CO_2 has a strong influence on the role of mass transport controlled by surface diffusion. The interaction of a inert atmosphere with the surface promotes oxygen vacancy formation, affecting surface diffusion or evaporation/condensation. Oxygen atmosphere inhibits the SnO_2 reduction decreasing the surface oxygen vacancy concentration. Some additives with lower valence at the sintering temperature form a metastable solid solution that creates extrinsic charged oxygen vacancies that promote mass transport at the grain boundary leading to densification and grain growth of this polycrystalline oxide. De-mixing of the solid solution during sintering results in two phases that could control grain growth of this ceramics.

SHAPING AND SINTERING OF CERAMIC NANOPOWDERS

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Nanopowders are composed of elementary particles (crystallites) of sizes smaller than 20 nm. Their heat treatment at temperatures lower than in the case of classical powders results in polycrystals of very small grain sizes. Such materials show improved mechanical properties. Although numerous methods of nanopowder preparation were elaborated, serious troubles in their processing are

still encountered, mainly due to the friction between powder particles. That is why dry pressing of such powders does not lead to satisfactory results. In the present work this will be exemplified using nanopowders in the yttria-zirconia system. A method of their synthesis under hydrothermal conditions will be described. The effect of the two forming methods, dry pressing and pressure filtration, on the powder behavior during sintering will be shown. The pore size distribution and microstructure of the material observation vs. its shrinkage will follow the system densification.

BULK AMORPHOUS AND NANOCRYSTALLINE ALLOYS

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The formation of bulk amorphous alloys by various methods has been introduced. The microstructural characteristics, phase transformations and glass transition of the best glass forming system $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk amorphous alloy under high pressure were systematically investigated using high resolution transmission electron microscope (HRTEM), differential scanning calorimetry (DSC), X-ray diffraction (XRD), ultrasonic study, and density measurements. The acoustic, thermal and elastic properties and their pressure dependence of various bulk amorphous alloys were studied. It was observed that high-pressure annealing induces phase separation and nanocrystallization below calorimetric glass transition. The role of pressure on structural relaxation and phase transition and the pressure dependence of the reversible and irreversible glass transition are discussed. Annealing of the bulk amorphous alloys under high pressure in the supercooled liquid region produces a composite with very fine nanocrystallites dispersed in the amorphous matrix. Nanocrystallization is pressure-assisted and complete nanocrystallization can be obtained by annealing under pressure. Pressure also controls phase selection during crystallization. The mechanism of pressure-assisted nanocrystallization is discussed.

PRINCIPLES OF THE FORMATION OF AMORPHOUS, NANO- AND MICROCRYSTALLINE ALLOYS

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The physical basics of nano- and microcrystalline alloy formation under superfast cooling of melts, raising dust, high-energy influence are explained. The conditions of nanoparticle creation and raising, structural particularities of amorphous and nanocrystalline binary and multicomponent systems are surveyed from the viewpoint of their phase changes, electronic structure, kinetic, thermal, magnetic and galvanomagnetic phenomenon. Ideas on clusters formation in materials of a different nature are presented. It is shown, that creation of mezoscopic quasi-equilibrium formations has an essential influence on physical properties of materials.

RATE-CONTROLLED SINTERING: APPLICATION TO NANOSTRUCTURED CERAMICS

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More than a decade has elapsed since the last review of rate-controlled sintering (RCS) was presented by professor H. Palmour III at the 7th Round Table Conference on Sintering and Related Phenomena in 1989. The phenomenology and description of the method was published in 1985 and earlier mainly in the work of H. Palmour III and collaborators. The methodology was transferred to industry and laboratory use and today's dilatometers provide RCS computer controlled regimes. Despite of all these achievements, few papers devoted to this outstanding example of high sintering technology appear. One decade of the author's efforts in RCS of nanostructured materials, both metals and ceramics, has brought a unique experience in this realm and new knowledge in the physics of sintering. New methodological details and experimental results of RCS of nanosized powders will be overviewed and some features of microstructure evolution will be presented and

compared with the conventional ramp-and-hold sintering and high pressure sintering widely used for consolidation of nanograined materials. The maximum safe rate and newly introduced minimum safe rate of densification are theoretically described. Both parameters were considered to be a result of the competition between shrinkage and grain growth under conditions of a variable heating rate.

NANOCRYSTALLINE ZIRCONIA POWDERS: CHEMICAL VAPOR SYNTHESIS AND SINTERABILITY

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Pure zirconia nanocrystalline powders have been prepared by chemical vapor synthesis, a modified chemical vapor deposition technique. The as-synthesized powders show an excellent crystallinity with a high specific surface area, small particle size and a narrow particle size distribution. Dense, nanocrystalline ceramics are obtained by normal and two-step vacuum sintering. Relative density up to 96 % of the theoretical density is achieved by vacuum sintering at 850°C for 20 hours. Fully dense ZrO_2 ceramics with the average grain size smaller than 60 nm, can be obtained only at somewhat higher temperatures. It was expected that two-step vacuum sintering could additionally suppress grain growth. However, from the present experiments, it can be concluded that this sintering schedule (efficient mostly for agglomerated nanopowders) does not result in suppressing of grain growth in zirconia pellets prepared from nanopowders exhibiting a small crystallite size, narrow particle size distribution and low degree of agglomeration.

THE NANOCRYSTALLINE BARIUM TITANATE CERAMICS: SYNTHESIS, SINTERING AND SIZE EFFECT

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Size effect is the defining factor in the development of electronic ceramics based on ferroelectrics and barium titanate, in particular. Prospects of application of nanocrystalline ferroelectric ceramics are based on new effects inherent to this class of materials due to changing of particle size of powders or ceramic grains. The basic properties are phase transitions and dielectric characteristics, which depend on the grain size. Reduction of grain size less than 1 μm causes changes in the ferroelectrics domain structure, reducing, in turn, the permittivity, and resulting in changes of phase transition temperatures, that superimpose a restriction on the following miniaturization of ceramic products. In order to make a nanocrystalline ceramics on the base of barium titanate, it is necessary to use up-to-date methods of syntheses and sintering, which take into account the competition of thermally activated mechanisms inherent to both syntheses and sintering. This paper presents results of non-isothermal rate-controlled synthesis and sintering of barium titanate by different methods, as well as the size effect revealed in nanocrystalline barium titanate. It is shown that the permittivity of barium titanate depends on effective width of grain boundaries, which consists of a physical grain boundary and a depolarization field area. The effective grain boundary width depends on ceramics consolidation methods. The permittivity of pure barium titanate can be equal to 5000 and does not depend on frequency and grain size in the range from 0.4 to 1.2 μm. The polydomain structure with a domain width of 10-12 nm is discovered in nanocrystalline barium titanate ceramics with a grain size of 50-70 nm. The generalized polymorphous phase diagram for pure barium titanate is proposed depending on the grain size and temperature.

RHEOLOGY OF SILICON NITRIDE AQUEOUS AND NONAQUEOUS SUSPENSIONS

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Stability of Si_3N_4 nanopowder suspensions of a different solid content (1 - 20 mass%), prepared in water and toluene, *n*-octanole and benzyl alcohol as organic dispersing media, was investigated via sedimentation tests and viscosity measurements. The isoelectric point of the Si_3N_4 powder was determined using ESA measurements. Rheological behaviour of aqueous suspensions was compared in regard to the Si_3N_4 content and the pH value applied for electrostabilisation. Rheology of *n*-octanole and benzyl alcohol prepared suspensions was compared with and without the presence of a deflocculant. Shear stress versus shear rate dependencies, fitted with the Casson model, have shown similar rheological behaviour of the aqueous suspensions in basic and acidic region, and expected increase of viscosity with increased solid content. Nonaqueous suspensions showed similar rheological behaviour and the best accordance with the Sisko model. It was shown that the presence of a deflocculant in the octanole prepared suspension has a remarquable influence on its stability.

THE TEMPERATURE OF MAGNETIC ORDERING IN ULTRATHIN MAGNETIC LAYERS

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A theoretical analysis of the influence and control of parameters of a thin multilayered system on the temperature of the phase transition into the magnetically ordered state is presented in the framework of mean-field approach [1]. Peculiarities of a structure consisting of the two different ferromagnetic films is analysed in detail. An opportunity of control of the transition temperature due to the thickness of the layers is revealed. According to the special relations between parameters of the system it would be possible, in particular, to shift the transition temperature below the Curie temperature of both layers. This phenomenon would occur due to the local magnetization gradients (under condition of non-zero total magnetization) originating from interlayer coupling and respective contribution to the free energy of the multilayer. The zero-magnetization state might become energetically favourable under special conditions. Relevant materials, further experimental investigations and possible applications are discussed.

1. V. Apalkov, Y. Boyko, V. Slezov, H. Worch, Z. Metallkd., **91** (2000) 3.

HIGH-MELTING POINT BULK NANOCOMPOSITES

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The sintering behavior of nanocrystalline titanium nitride powders and TiN based composites has been studied under both linear and rate-controlled heating regimes in vacuum, hydrogen and nitrogen. The non-linear temperature-time path of RCS results in a more uniform grain structure than a linear heating schedule during sintering. The final grain size around 50 nm and residual porosity less than 2 % is the best evidence of RCS advantages over the linear heating rate regime (600-1100 nm grain size and ~6 %, respectively). The near fully dense and fine-grained rate-controlled sintered specimens demonstrated the highest hardness ~26 ± 1.3 GPa and fracture toughness 4.2 ± 0.2 MPa· $m^{1/2}$. The dependence of hardness on the heating rate, grain size, porosity and regime of sintering is a result of the present investigation.

FEATURES OF THE BEHAVIOR OF TITANIUM NITRIDE NANOPOWDERS DURING SINTERING UNDER THE CONDITIONS OF HIGH PRESSURES

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The formation of a nanocrystalline structure in a sintered material provides preparation of ceramic products with improved physicomechanical properties. Different processes of consolidation of nanopowders, that enable prevention of a significant increase in the size of starting particles and obtainining of a sintered polycrystal with a grain size under 100 nm, are known. Sintering under high pressures is among these. By now numerous investigations of sintering of materials by this method have been carried out. However, the currently available information does not reveal the features of the effect of quasi-hydrostatic compression under high pressures on the evolution of the substructure of grains depending on their size. In connection with this, a comparison of the effects of the action of high pressures on powders with the initial particle size of about 60 μn obtained by synthesis in a furnace and plasmochemical nanopowders with a size of 70 nm is made. Experiments were performed on a high-pressure unit based on a hydraulic press with a force of 6300 kN. A lens-type pressure chamber (PC) with a diameter of the working channel of the cell of 9 mm was used. Experiments were carried out in the pressure range 2-5 GPa at a temperature of 293 K, and in the temperature range 1273-1773 K. The sintering time was minimized in view of the necessity to preclude the effects of decreasing pressure during the sintering cycle that are caused by shrinkage of the material of the PC cell, and limit the process of grain growth during sintering. The total sintering time did not exceed 1.5 min. The temperature was raised linearly, and, at its maximum value, an exposure lasted for no more than 20 s. An X-ray diffraction analysis of sintered materials was performed on a DRON-3M diffractometer. Parameters of the fine structure of the material were calculated from the broadening of diffraction lines. Hardness was measured on a PMT microhardness tester. The density of sinters was determined by hydrostatic weighting. The range of used pressures was chosen from the

condition of the necessity of deforming the frame of a powder body during generation of a high pressure and in the process of sintering. It was proposed to use the Hubert–Mises condition in consideration of the deformation process under high pressures. We proceeded from the assumption that, on the free surface of a pore, the material is in a plane-strained state. For this case, the instant of deformation comes as the relationship $\sigma_{mean} \geq 2\sigma_0$ is satisfied, where σ_{mean} is the mean hydrostatic pressure produced in the working volume of the PC; σ_0 is the compression strength of the sintered material. For titanium nitride, this relationship is as follows: $\sigma_{mean} \geq 2$ GPa. Specimens of the specified shape (5 mm in diameter and 4 mm in height) were sintered in the indicated pressure range. X-ray diffraction analysis data show that splitting of the regions of coherent scattering (RCS) proceeds even at room temperature, and, in nanopowders, their size is two orders of magnitude smaller than in micropowders after action of a pressure of 3 GPa. Nevertheless, the residual microstresses of the crystal lattices of both types of powders are close in value ($\Delta a/a = (20\text{-}33)\times10^{-4}$). As temperature and pressure are raised, the characteristics of the substructure change insignificantly. It should be noted that microstresses in nanopowders are always higher than those in micropowders. The causes of this phenomenon were considered. It was established that the microhardness of compacts from nanopowders was 24-26 GPA and the microhardness of compacts from micropowders was not more than 20 GPa. Thus, the features of the effect of high quasi-hydrostatic pressures on titanium nitride powders with different particle sizes were determined.

THERMAL BEHAVIOUR AND STRUCTURAL PHENOMENA OF NANOPHASED ZnO POWDERS

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Thermal behaviour of nanophased ZnO powders was investigated using differential scanning calorimetry performed under linear heating conditions, with

heating rates of 5, 10, 15 and 20°/min. The nature of the observed exothermal heat effect in the temperature range from 386 to 498°C was correlated to the particles structural data obtained by SEM, TEM and x-ray analysis. As a theoretical base for the description of quasi-nucleation and crystallite growth processes, the Johnson Mehl-Avramy equation was applied. Nanophased ZnO powders are obtained through two different synthesis techniques: ultrasonic spray pyrolysis of 0.8 mol/dm^3 nitrate solution and subsequent decomposition of 2.7 μm droplets in the temperature range up to 600°C; and high energy vibro milling of ZnO powders in the duration of 300 min. The primary crystallite size in particles before heating was under 30 nm for both samples.

ELEMENTS OF THE FORMATION OF NANOSIZED PARTICLES BY CVD UNDER A LAMINAR REGIME

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A concept of formation of nanosized particles by CVD will be presented in the light of laminar transport phenomena. Two essential steps: (I) nucleus formation and (II) nucleus growth will be explained from the theoretical point of view. Also, three basic types of particles (i) semi-homogeneous (nucleus core with same surface layer); (ii) "simple" heterogeneous (nucleus core with different surface layer produced by "simple" CVD) and (iii) heterogeneous (nucleus core with different surface layer produced by surface chemical reactions during the CVD), will be discussed. An experiment of "simple" heterogeneous particle formation will be described as an example of the presented theoretical approach.

PECULIARITIES OF THE STRUCTURE AND BIOLOGICAL ACTIVITY OF ULTRA DISPERSED (NANO) IRON POWDERS

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The paper shows the advisability of applying ultradispersed (nano) powders (UDP) of iron as a biologically active preparation in Plant Growing and Live Stock Farming. It was defined by the method of electron microscopy of high resolution that nano-particles (NP) of iron, obtained at applying chemical-metallurgical method, represent metal nucleus from α–Fe, covered by solid oxide layer of 5.0 nm, containing the forms of FeO, Fe_2O_3 and Fe_3O_4. With this, value of lattice parameter of UDP of alpha-iron, determining by the method of X-ray structural method, is higher than that of compact iron. Nano-particles possess crystal-graphic cut, and they are truncated along axis "Z". The biologically active preparations were prepared on the basis of UDP of iron. Introduction of suspension, even under-doses of approximately 10^{-30} g/ml, showed efficiency of its (suspension) application in Plant Growing on the example of tomato seeds germination. Positive results were also obtained in preliminary experiments on investigating the influence of UDP of iron (in suspension) on organisms of healthy and those infected by BLV of animals.

POWDER SYNTHESIS AND PROCESSING

COMPARISON OF SOFT MECHANOCHEMICAL AND SOL-GEL METHODS OF PREPARATION OF DISPERSED OXIDE MATERIALS

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The soft mechanochemical synthesis of inorganic compounds is a promising method in chemistry. It is realized in high-intensity grinding equipment; highy reactive solid acids, hydroxides, hydrated oxides, acid and basic salts are used as starting materials. Nucleation of new phases can be generated in mixtures of these solids by mechanical activation in highly-intensive grinding devices. Local temperatures and pressures arising during this treatment provide the formation of these nuclei at the contacts between the reagent particles. The interaction between initial components can lead to the formation of intermediate compounds, which can decompose during thermal treatment to give either new compounds or substances. In this study the results of the preparation of dispersed powders composed of aluminum, titanium, zirconium oxides by means of mechanical activation followed by thermal treatment are presented. Al_2TiO_5 is usually obtained by long sintering of mixtures of aluminum and titanium oxides at temperatures above 1400°C. We obtained it by mechanical activation of a mixture of aluminum hydroxide and metatitanium acid followed by thermal treatment at 1340°C for 6h. It was shown, that mechanical activation of this mixture results in the formation of a double hydrated compound. The formation of crystalline $ZrTiO_4$ from mechanically activated hydrated zirconium and titanium oxides occurs within the temperature range of 400-600°C. It is also shown, that the range of optimal content exists for the synthesis of $ZrSiO_4$ from mixtures of hydrated oxides followed by thermal treatment at 1200°C. A maximum product yield can be obtained within this range. The same theoretical explanations about the nature of chemical interactions during mechanical activation are proposed.

SYNTHESIS AND APPLICATION BY MECHANICAL ALLOYING

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For more than half a century scientists have been using the mechanical alloying technique (MA) in order to synthesize new materials with new properties that cannot be create by the conventional route e.g. due to a not present thermal equilibrium or immiscibility of their components. By structural design, important materials properties can be influenced (e.g. nanocrystalline, amorphous). If the same technique is applied for particle size reduction and/or particle deformation of single-systems e.g. to receive a special particle geometry, this route is to be described as High Energy (ball) Milling (HEM) and is suitable for rapid and large-scale production of ductile metal-flakes in dry process without solvents and less energy e.g. for paint-pigments, conductive pastes and anti-corrosives. On the contrary rapid particle size reduction of brittle solids like Enamels or Glass Fluxes has recently been introduced as a new application field. By Reactive Milling (RM), ultra-fine (nanoscaled) dispersions of particles/grains in a matrix can be achieved which can additionally be cost/energy saving due to a cheaper starting material that is transformed by chemical reaction in a direct/shorter route. Environmental concerns play an important role in the field of solid state synthesis where e.g. organic solid-solid reactions can rapidly proceed without wastes in the absence of solvents. However it has not been possible, except in a very limited number of more less exotic applications, to really commercialize the in principle cheap processing technique(s) for large scale products. Either the material-systems itself are focused on high-tech products of to far future and/or focused on covering to many advanced properties at the same time and are therefore too expensive or simply not demanded for present large scale production or the potential of a scaled up large production is not seen, so the market for the material would be there but not for the technique since its sufficient capability is not expected or known. This has been the main motivation for Zoz GmbH to approach PM-production about 4 years ago with materials made by MA, HEM and RM which is usually related to powder materials for coatings or later consolidation and recently did lead to

functional PM-bulk-parts. The present paper explains the process principle in particular with respect to large-scale application, the natural advantages of the collision-route in high kinetic processing and gives a survey of the current PM-production by this technique. This will cover powder materials for coatings, advanced bearing bushes by MA/HIP for liquid metal application, an advanced NdFeB-magnetic filter system as well as a continuously operating pilot plant with insitu separation and classification currently used for the processing of enamels and glass-fluxes. Materials-characteristics will be given by SEM, XRD, TEM, laser diffraction and chemical analysis.

MECHANICAL ACTIVATION OF SINTERING OF W-BASED HEAVY ALLOYS

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The mechanical activation of sintering of W/Ni/Fe, W/Ni/Co, and W/Ni/Cu heavy alloys with a concentration of W from 80 to 95 wt.% was investigated. The mixtures of powders of the elements were subjected to mechanical treatment in inert atmosphere. Then, the powders were pressed at room temperature and annealed in vacuum or hydrogen environment. The methods of X-ray diffraction, SEM and optical microscopy, local X-ray fluorescence analysis, and measurements of density and porosity were used for characterisation of the initial powders, powders after mechanical activation, green compacts, and tablets annealed at different temperatures. In addition, the mechanical properties (hardness, compression and shear tests in static and dynamic conditions) and fractopraphy data were analysed for sintered samples. The mechanical activation of tungsten based compositions with small additions of plastic metals is accompanied by accumulation of defects in W and deep intermixing of the components. The steady stage size of microblocks in W under mechanical treatment becomes close to 20 nm, and the value of microdistortions is close to 1 %. The W particles after

activation are 0.3-0.5 μm in sizes and are uniformly covered with a thin layer of Ni and Fe (or Co, Cu). An optimal dose of mechanical treatment is equal to 7-10 kJ/g. As a result, mechanical activation significantly accelerates the following processes of relaxation and compacting. Recrystallization of the tungsten defective crystal structure is appreciably completed even at 800°C. Annealing at 1100°C is accompanied by significant compacting of W/Ni/Fe samples and reaches 95 % of the theoretical density. Heating in hydrogen atmosphere at 1300°C results in practically complete sintering of the 93W-5.6Ni-1.4Fe specimen (99 % of the theoretical density). Thus, the use of the mechanical activation method enables one to obtain dense alloys by solid phase sintering. As the temperature of the solid phase sintering grows, the tungsten grains aggregate, while nickel-iron layers concentrate on the surface of the aggregates. Later on, the aggregates become enlarged, and their volume is depleted of nickel and iron resulting in the formation of the common tungsten alloy structure, i.e. tungsten grains with sizes close to tens of microns are covered with nickel-iron layers. Nevertheless, the sub-structure with characteristic sizes of 0.3-0.5 μm remains in the large tungsten grain. This sub-structure corresponds to tungsten particles prepared during mechanical activation. The structure and mechanical properties of (93 – 95 wt.%) W/Ni/Fe(Co) alloys, sintered at 1300 and 1500°C as well as (80-95 wt.%) W/Ni/Cu, sintered at 1200°C will be presented in detail. The use of the method of mechanical activation enabled a decrease of the sintering temperature, lowering of W grain sizes and preparation of alloys with unusual plastic properties.

DEFECT FORMATION AND THERMAL PROCESSES DURING MECHANICAL TREATMENT OF DISPERSE SYSTEMS

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An analysis of regularities of defect formation and development of different impulse and accumulate thermal processes during mechanical treatment of disperse systems is carried out. The existence of close intercoupling between these processes and the properties of obtained materials produced by mechanical treatment is shown. The responsibility of mechanothermal processes and processes of defect formation for the development of mechanochemical reactions, the so-called "cold sintering" etc. is discussed. The capabilities of practical use of discussed phenomena are reviewed.

DIMENSION AND STRUCTURAL CLASSIFICATION OF PARTICLES IN POWDER METALLURGY

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In practical Powder Metallurgy the following gradation of particle dispersion has been accepted:

a.	0.001–0.1 μm	Ultra Disperse Powders (UDP);
b.	0.1–10.0 μm	Fine Disperse Powders (FDP);
c.	10.0–200.0 μm	Avarage Disperse Powders (ADP);
d.	Over 200.0–1000.0 μm	Course/Large Disperse Powders (C/LDP).

Taking into consideration numerous experimental results of investigations of the structural formation of different dimension powder groups, the below-mentioned particle classification is suggested:

1. powders, possessing polycrystalline structures such as:
    a. C/LDP of reduced and atomized/dispersed iron;
    b. FDP of electrolytic and atomized/dispersed nickel.
2. powders, having a fragmentary structure such as:
    a. FDP of carbonil nickel, tungsten, molybdenum as well as the powders of sub-micron dimensions 0.1–1.0 μm;
3. powders, possessing a nano-crystalline structure such as:
    a. FDP, obtained by the method of spray-pyrolysis and UDP metals disposed to twinning;

4. powders, having mono-crystalline structures such as:
    a. UDP of metals not disposed to twinning and oxides, representing, as it were, one and the same "field" of coherent dispersion with an average dimension less than 10.0 nm.

The given classification is useful both for practical and for scientific activities in research processes for consolidation of powders of different dispersing degrees.

PHYSICAL-CHEMICAL, STRUCTURAL AND PHASE TRANSFORMATIONS DURING THE PRODUCTION AND COMPACTING OF ATOMIZED FERROUS POWDERS

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During the process of producing ferrous powders, atomized by water and air, as well as during further sintering of pressed samples on the basis of obtained ferrous powders, the influence of the particle surface on the structure formation process in the course of compacting/consolidation was noticed. Thus, when obtaining atomized powders, the formation of their ferrite poly-crystaline structure with uneven grain boundaries is conditioned by physical-chemical, structural and phase transformations:

1. in small volumes, limited by particle dimensions (50 - 160 μm);
2. in parallel with active diffusion removal of carbon from particle volume by oxygen in oxide layers, the depth of which make units to tens of microns;
3. under the action of thermal tension along the inter-phase boundary "Me - MeO;
4. for limiting migration of grains boundaries under the influence of non-metallic inclusions into the particle volume;
5. for phase hardening at uneven phase over-crystallization from the particle periphery to their center.

Probably the centers of gem formation, being placed, in the main, at a inner side of the upper layers of the particles, are preserved in the course of further non-isothermal sintering of pressed samples in hydrogen. These centers form structures

during the development of intro- and inter-particle re-crystallization, and also phase "alpha-gamma" over-crystallization. As a result of the above the initial size of grains and character of their dimension-wise distribution is restored in non-isothermally sintered pressing. This phenomenon is called "structural heredity" (1-3).

OBTAINING HIGH-DENSITY MATERIALS ON THE BASIS OF RESTORED AND ATOMIZED FERROUS POWDERS BY THE METHOD OF MAGNETO-IMPULSE PRESSING

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In [1-2] the high effectiveness of magneto-impulse pressing during synthesis of a number of ceramics with fine structure received from nano-dimension powders was shown. In this paper magneto-impulse pressing was applied for producing a high-density material on the basis of restored as well as water- and air-atomized ferrous powders. However, this is not powder, but preliminarily sintered pressing with a given porosity that was exposed to magneto-impulse pressing. The investigations showed that billets, received from air-atomized ferrous powder, possessed a higher density (98 % and over) and better mechanical properties.

1. V.V. Ivanov, Synthesis of ceramics received from nano-dimension powder Al_2O_3, pressed by magneto-impulse method, Inorganic Materials, **34** (4) (1998) 39-43. (in Russian)
2. G. Link, V.V. Ivanov, S. Puranin, V. Khrustov, R. Buhme, Mater. Res. Symp. Proc., Vol 430, 1996, p. 157-162.

MECHANOACTIVATION OF CHROMIUM SILICIDE FORMATION IN THE SiC – Si – Cr SYSTEM

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The methods of X-ray, IR-spectroscopy, electron microscopy and X-ray microanalysis were used in the research of the reaction processes during mechanical treatment of a SiC-Cr-Si mixture and its subsequent temperature treatment in the temperature range of 1073 - 1793 K. It was established, that during mechanical treatment of the mixture chromium silicides are formed. Thermal treatment completes the given process. Silicide formation is realized in the framework of the diffusion of silicon in chromium. During the presence of SiO_2 in the mixture silicide formation occurs also as the result of silica reduction by silicon and silicon carbide. Sintering of synthesized composite powders of SiC - chromium silicides at high temperature and pressure (T = 2073 K, P = 5 GPa) is accompanied by the destruction of α-SiC particles, α→β transition in silicon carbide and by deformation distortions of chromium silicide crystal lattices.

HYDROTHERMAL SYNTHESIS OF SOME IRON OXIDES. STRUCTURAL AND MAGNETIC PROPERTIES

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Hydrothermal synthesis was used as an alternate method for the preparation of ceramic materials. Some practical and theoretical aspects of the

experiments we carried out to obtain iron oxides by hydrothermal route are presented. By changing the nature of reactants, temperature, heating rate, treatment time, etc., iron oxides with various compositions and morphology were obtained. Thus, hematite powders with a desired particle shape (needle like, polyhedral, plate like, spherical, hexagonal) and dimension (0.1–30 μm) were prepared by hydrothermal synthesis in the temperature range of 160–300°C, using goethite or ferric hydroxide as precursors. The reaction kinetics of the hydrothermal transformation goethite → hematite was studied by means of Mössbauer spectroscopy. Polycrystalline spinel ferrites $Fe_{3-x}M_xO_4$ (M^{n+} = Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}; $0 < x < 0.375$) were synthesized by hydrothermal treatment of aqueous ferrous / M-hydroxide suspensions (obtained by coprecipitation with sodium hydroxide from Fe^{2+}/M^{n+} sulphate solutions, under controlled pH-conditions). A reaction mechanism under hydrothermal conditions is proposed. The structural, morphological and magnetic properties of hydrothermaly synthesised oxides were investigated by X-ray, Mössbauer spectroscopy, electron microscopy and magnetic measurements. The potential applications of hydrothermally synthesised magnetic iron oxides are discussed.

INFLUENCE OF THERMAL TREATMENT CONDITIONS ON THE PHASE COMPOSITION OF PMN CERAMICS PREPARED BY MECHANOCHEMICAL SYNTHESIS

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PMN powders of the $Pb(Mg_{1/3}Nb_{2/3})O_3$ composition were prepared by mechanochemical synthesis. X-ray analysis confirmed the presence of a perovskite phase with traces of carbonates and a pyrochlore phase. To eliminate undesired phases, PMN powders were treated at different calcination temperatures before

sintering. It was found that the phase composition and density of final ceramics was dependent on combinations of calcination and sintering temperatures, suggesting a necessity of simultaneous optimization of these parameters.

MECHANICAL ALLOYING OF COPPER WITH COMERCIAL ALUMINA PARTICLES

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The mechanical alloying of copper with 1.5, 2.5 and 5 wt.% Al_2O_3 has been carried out in a planetary ball mill in air for various milling times (0, 3, 5, 10 and 20 h). All powders were treated in H_2 at 400°C for 1 h, in order to eliminate formed oxides. Hot pressing was used for compaction (800°C, 3 h, Ar). High energy milling effectively reduces the grain size of treated powders. A typical lamelar structure, with Al_2O_3 particles largely restricted to interlamelar planes between adjacent copper lamellae formed in the early stage of milling. This structure was retained after compaction as well. Microhardness measurements showed a progressive increase with milling time and an increase in the alumina content up to 2.5 wt.%. After 10 h of milling, the microhardness of Cu + 2.5 wt.% Al_2O_3 was 2 times higher than that of the as-received electrolytic copper compacted under the same conditions.

PROCESSING OF ALUMINA CERAMICS WITH ACRYLATE BINDERS

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Alumina tehnical ceramics products with complex shapes can be manufactured by green machining, so that the final costly diamond machining of

sintered parts is significantly reduced. In this paper the possibility of using acrylates (monomer and polymer) as a binder in the multicomponent mixture of alumina powder and organic additives (deflocculant, binders, plasticizers) was investigated. The infuence of different pressures (up to 147 MPa) on green density and machinability was investigated for different compositions, ranging up to 4 mass% of the acrylate binder. After standard heat treatment near glass transition temperature (115°C) for activation of functional groups and at different temperatures for monomer polymerization pressed parts were characterized and machined. Green density, as well as machining, is dependent on the composition (acrylate monomer or polymer) and pressing pressure. Addition of acrylate can improve green density by 5 % and significantly machinability (lathing, milling, drilling, channel indentation as well as the indentation of the outside and inside tapping).

AEROSOL SYNTHESIS OF $LiMn_2O_4$ THIN FILMS AND THEIR ELECTROCHEMICAL PERFORMANCES

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$LiMn_2O_4$ thin films were obtained by aerosol synthesis through the Pyrosol process. Precursor solutions were aqueous lithium and manganese nitrates with the Li/Mn stoichiometric ratio of 1:2. Concentration of precursor solution ranged from 0.1 to 1 mol/dm^3. Physicochemical properties such as surface tension, viscosity, pH and concentration were measured, and then the mean diameter of aerosol droplets was calculated. It varied from 2 to 9 microns. The starting solution was atomized by an ultrasonic generator at the frequencies of 800 kHz and 2.5 MHz. Substrates for thin film deposition were metal Ti and carbon glass. Deposition was held at temperatures ranging from 573 to 1173 K, in air with controlled flow rates. The crystal structure was revealed by X-ray diffraction (XRD), morphology was determined by scanning electron microscopy (SEM) and electrochemical properties in terms of cycle performance were discussed.

PROPERTIES OF $BaTi_{1-x}Sn_xO_3$ FUNCTIONALLY GRADIENT MATERIALS DEPENDING ON THE METHODS OF POWDERS PREPARATION

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Barium titanate ($BaTiO_3$) ceramics have great industrial importance and wide applications as capacitor materials and PTC (positive coefficient of temperature) devices where $BaTiO_3$ is doped with some additive. Various substances are usually added to optimize the properties of basic ceramics. In our work we used SnO_2 as an additive for the basic $BaTiO_3$ powder and prepared $BaTi_{1-x}Sn_xO_3$ powders with different Sn contents (0 - 15 mol.%). Two different methods of $BaTi_{1-x}Sn_xO_3$ preparation were used. In classical mechanochemical synthesis starting $BaCO_3$, TiO_2 and SnO_2 powders are mechanically activated. After several hours of their activation $BaTi_{1-x}Sn_xO_3$ powders are prepared. In the second method we used a commercial $BaTiO_3$ powder and SnO_2, which were homogenized in ethanol. After homogenization the powders were dried and $BaTi_{1-x}Sn_xO_3$ was obtained after calcination at 1100°C for 1 h. The prepared powders were pressed into pellets, which contained 2 - 4 layers with different SnO_2 contents. Every layer was 400 μm thick. The powders were pressed uniaxially into pellets of 3.9 g/cm^3 in density. The samples were sintered by heating at 1370°C for 2 h, in air. Every powder obtained by the two different methods and the final ceramics prepared by powder pressing and sintering were characterized by X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM).

POSSIBILITY OF CHARACTERIZATION OF POWDERS USING A HORIZONTAL COHERER

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The possibility of characterization of Al, Cu, InS and PbS powders using a horizontal coherer has been considered. The powders of known dimensions were treated with a high frequency electromagnetic field or with a DC electric field, which were slowly increased until a dielectric breakdown occurred. The activation time of the coherer was measured as a function of the powder dimension using a PC-428 Electronic Design multifunctional card and a suitable interface between the coherer and PC. Finally, it was shown that the average dimension of powders of unknown size could be determined using the calibrated horizontal coherer.

INFLUENCE OF PARAMETERS OF MECHANOCHEMICAL TREATMENT ON REACTION KINETICS – EXPERIMENTAL AND THEORETICAL APPROACHES

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The influence of parameters of mechanochemical treatment in a laboratory high-energy planetary ball mill on reaction kinetics of different high exothermic systems was followed by hardened-steel vial wall temperature measurements. Increasing of the rotating rate of the supporting disc, as well as, increasing of the ball-to-mass ratio, increases the reaction rate. Increasing of the ball diameter above a certain size, induces increasing of the reaction rate.

FUNDAMENTAL PROBLEMS OF PROCESSES IN THE TECHNOLOGY OF SILICATE MATERIALS

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The development of advanced technologies of silicate materials is connected with resolving a series of fundamental problems of solid-state physics and chemistry. They represent the basis of modern science of sintering. This paper deals with general problems of reaction and liquid-phase sintering of silicate systems. The sintering mechanism of kaolin was analyzed. It can represent the basis for understanding processes occurring during heating of silicate systems. Practical applications of results obtained from fundamental research have also been given.

SINTERED ADVANCED MATERIALS

THE DESIGN OF BORON CARBIDE-BASED INFILTRATED CERMETS

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The outstanding properties of B_4C have made it a choice ceramic for many applications in which hardness, wear and corrosion resistance and very low specific weight are of paramount importance. Widespread use of this material is limited, however by the intrinsic brittleness associated with its strongly covalent bonding. Boron carbide based ceramic-metal composites have been considered in order to increase the toughness. One common approach for the production of such composites is the infiltration of a partly sintered B_4C preform by a molten metal, most often, aluminum. Pressureless sintering of pure B_4C takes place at elevated temperatures and is often associated with excessive grain growth. Various additives such as free carbon have been used in order to improve sintering of B_4C. For the preparation of B_4C-Al composites, however, the main drawback of this approach is the potential appearance of deleterious Al_4C_3, whose presence may cause the gradual destruction of the composite material. Metals, other than Al, may, in principle be considered as an alternative in B_4C-based composites. Unalloyed copper does not wet B_4C and has to be alloyed in order to infiltrate the porous ceramic preform. Silicon is, in principle, an appropriate alloying additive to copper because it improves the wetting and allows infiltration and may, as the outcome of a subsequent reaction with B_4C, lead to the *in-situ* formation of some SiC that should improve the final hardness of the composite. Unfortunately, SiC forms at the surface of the B_4C particles, forms an inpenetrable barrier and precludes further reaction between the metal and the ceramic matrix, even in the course of extended heat treatments. The addition of some ferrous metal, Me= Fe or Ni , to the melt allows overcoming of these limitations. The presence of these additives greatly increases the solubility of carbon in the (Cu,Si, Me) melt and allows the subsequent formation of SiC throughout the metallic phase of the composite material. The experimental results and some details of the thermodynamic background of this relatively complex procedure of material design will be presented and discussed.

ON THE SINTERING OF THE HfC-TiC AND (Hf,Ti)C POWDERS

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A mixture of HfC and TiC powders and a (Hf,Ti)C powder have been hot pressed with and without 4 wt.%Ni. In the absence of Ni the hot pressing temperature was 2000°C and in the presence of Ni it was 1650°C. The pressure was 50 MPa in both cases. The starting powders were substoichiometric, as deduced from XRD spectra analyses, and the (Hf,Ti)C powder consisted of a range of compositions, as indicated by the width of the XRD peaks. In the absence of Ni the powders sintered without the formation of a liquid phase. In the case of the HfC and TiC mixture sintering occurred with simultaneous formation of a (Hf,Ti)C solid solution. On account of the mutual solid solubility of the two carbides vacancy interdiffusion controlled the solution as well as the sintering process, assisted by the high concentration of vacancies in the starting powders. In the case of (Hf,Ti)C powder diffusion was also the controlling process because the solid solution was not homogeneous and the system tended to homogenization, as shown by the narrowing of XRD peaks after sintering. Since the diffusion of HfC into TiC did not occur at the same rate as the diffusion of TiC into HfC (as expected, on account of the different melting points of the two materials) diffusional porosity was observed in some (Hf,Ti)C grains. Grain growth was substantial but uniform. In the presence of Ni, sintering occurred with the formation of a liquid phase. The volume fraction of the liquid phase formed was sufficient to yield a low porosity. Grain growth was less than in the case of material sintered without Ni, possibly just on account of the lower sintering temperature.

STRENGTHENING OF SINTERED MATERIALS

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Possible ways to improve mechanical properties of porous materials depending on the volume fraction of pores are discussed. The first possibility is an enhancement of fracture toughness of the porous material with increasing of the volume fraction of pores. The second is the growth of relative stiffness of high-porous systems. The third case is to increase absorbing capacity of strain energy at high porosity. The sensitivity of these effects to the morphology of porous space and structure of a solid phase is analyzed. The methods of structure optimization in order to obtain maximum effects are proposed. Solid state structure and porous space morphology were taken into account. There is a good agreement between theoretical calculation and experimental data. Requirements of designers will always be met if the morphology of the porous structure and mechanical properties of the basic metal is optimal.

CORDIERITE STRENGTHENING WITH SIMPLE AND COMPLEX OXIDES

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The influence of simple oxide additives (TiO_2, ZrO_2, Nb_2O_5, WO_3) and complex ones ($3Al_2O_3$ $2SiO_2$, Al_2TiO_5, $ZrSiO_4$) on the strength of cordierite ceramics is investigated. It is stated that the compression strength increases in the presence of oxides. For the oxide content of 20 - 30 mol.% (5 - 7 mass%), compression strength increases 1.5-2 times. The presence of simple oxides causes an increase of the mullite phase content of cordierite; no such increase is observed in the presence of complex oxides. In the presence of additives, cordierite ceramics is fine-grained, low- porous and contains a smaller number of micro-cracks.

THE INFLUENCE OF THE ATMOSPHERE ON THE SINTERING OF SILICON NITRIDE

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Silicon nitride ceramics, like many other nonoxide ceramics, show an intensive interaction with the atmosphere during densification. These interactions are mostly caused by the limited stability of the oxide nitride additives under sintering conditions and by the presence of a carbon heater and crucibles in the commonly used furnaces. These reactions influence not only the densification but also the formation of the microstructure and coloration of materials. The interactions and their influence on the densification, microstructure and colour will be analysed and explained on the bases of thermodynamic considerations and experimental data.

SINTERING AND COMPOSITION OF SAMPLES MADE FROM FINE AL_2O_3 AND β'-SIALON COMPOSITE MADE FORM BAUXITE

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The sintering and composition of samples made of a powder mixture consisting of fine α-Al_2O_3 powder and β'-Sialon composite powder which was made form bauxite by carbonthermal reduction and nitridation were studied. The samples had the diameter of 20 mm and height of 20 mm, 2 wt.% MgO was added for improvement of sintering. The samples were sintered at 1600° for a soaking time of 4 h and 8 h in N_2 atmosphere. The main conclusions are drawn as follows:

1. With increment of the content of β'-Sialon composite powder the apparent porosity, relative density of the samples sintered at 1600°C decreases and increases, respectively;

2. The relative density and shrinkage during sintering of the samples increase with increment of the soaking time. The higher the content of β'-Sialon composite powder in the powder mixture, the larger the effect of soaking time;
3. After sintering at 1600°C, α-Al_2O_3, 15R and MgO disappear in the samples made of β'-Sialon composite powder without addition of fine α-Al_2O_3 powder. In the samples made of the powder mixture consisting of 60 wt.% β'-Sialon composite powder and 40 wt.% fine α-Al_2O_3 powder, β'-Sialon, α-Al_2O_3 and MgAlon coexist.

NEW BARRIER CERAMICS FOR MELT TECHNOLOGIES OF HTSC MATERIALS

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In order to identify prospective candidates for new barrier materials for melt processing of HTSC ceramics and single crystals, a series of binary and ternary perovskite-like oxides (Y)$BaMO_3$ (M = Ce, Th, Ti, Hf) has been investigated. $BaCeO_3$ and $BaHfO_3$ demonstrated outstanding chemical resistance comparable to the one of $BaZrO_3$. Introduction of small amounts (0.5 – 5 %) CuO and/or $BaCuO_2$ substantially enchances the sinterability of $BaMO_3$ (M = Ce, Zr, Hf) powders obtained by solution processing methods while contamination of the HTSC melt by alien cations during further processing is avoided. The character of densification curves and dopant distribution in the $BaMO_3$ matrix undoubtedly shows a liquid phase mechanism of sintering acceleration. Neither chemical degradation nor solubility of $BaZrO_3$, $BaHfO_3$ and $BaCeO_3$ ceramics in Y(RE)-Ba-Cu-O melts have been observed during melt processing experiments. Meanwhile outstanding wetting ability of these melts at high temperatures leads to their physical penetration even to tiny pores, so that open porosity in barrier ceramics should be eliminated. Fully dense protective coating, resistant to the melt penetration, can be created on $BaMO_3$ ceramics (M = Zr, Hf, Ce) by RF plasma processing of their surface at normal pressure.

SINTERING OF TITANIUM BASED COMPOSITIONS WITH INORGANIC COMPOUNDS OF VARIOUS PHYSICO-CHEMICAL NATURE

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In the context of high titanium chemical affinity to elements forming refractory inorganic compounds, diffusion - reactionary processes were observed during sintering titanium compositions resulting in active consolidation in most cases. This occurs during sintering of titanium compositions with carbides of metals of IV, V and VIA groups over a wide concentration range. Carbides of transition metals of VIA group activate the sintering process most effectively. Doping with covalent compounds (B_4C, BN, AlN etc.) up to 20 vol.% also results in an increase of shrinkage and fall of the sintering temperature. During sintering of titanium with oxides the activation effect is most expressed in the case of thermodynamically low-strength metal oxides compared to titanium oxide. The submitted systems belong to a class of temporary-excited systems, which relax to an equilibrium state during sintering. For such systems the dependences of volume changes on the sintering temperature have one maximum as a rule.

SINTERING OF POWDER REACTIONARY SYSTEMS WITH A DYNAMIC CHARACTER OF STABILITY

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The practical development of ideas of non-equilibrium thermodynamics and synergetics enabled creation of compositions on the base of inorganic systems with self-organizing elements. The self-organizing phenomena occur during sintering as a result of the non-linear mechanism of interactions caused by joint diffusion processes, competitive reactions with catalytic and autocatalytic stages, phase transitions and accompanying thermal effects. During sintering the self-

organizing compositions keep non-equilibrium and related excitation concerning external energy flows. Evolution during sintering of such systems is followed by a cascade of bifurcations, resulting in volume changes of a non-monotonous character. Owing to collective transport of components in the reacting system extensive temperature-temporary areas of active sintering exist, especially in coarse-dispersed compositions.

INFLUENCE OF HIGH PRESSURE ON THE PECULIARITIES OF REACTION SINTERING OF MATERIALS BASED ON BORON CARBIDE

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Using high pressure is expedient for producing high-strength materials from powders of refractory covalent compounds. Our investigations have shown that under the influence of high pressure the conditions of powder consolidation change. It accelerates sintering processes that take phase at lower temperatures. Using high pressure is especially effective in the process of hard-phase reaction sintering, where the forming compounds have a larger density. In particular, it concerns the system B_4C-MeC, when during the process of reaction sintering materials on the base of B_4C-MeB_2 are formed. Indeed, the elementary cell volumes of formed boride phases are significantly smaller than the ones of initial carbide phases, e.g., the elementary cell volume of TiC is 0.0810 nm^3, of ZrC it is 0.1036 nm^3, of TiB_2 it is 0.0258 nm^3, and of ZrB_2 it is 0.0310 nm^3. In this work, the interaction of boron carbide with titanium, zirconium and vanadium carbides in various thermobaric conditions is studied. Promising compositions of initial mixtures are determined. The obtained composite heterophase material on the base of B_4C-MeB_2, has a disperse structure and is distinguished by high hardness of 42-45 GPa.

SINTERING IN SHOCK WAVES OF A HARD ALLOY-DIAMOND COMPOSITE

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An analysis of factors determining the level of properties of sintered composite hard alloy - diamond materials was performed. It is shown that, in order to improve the physicomechanical properties of these materials, the damageability of diamond grains and the stress concentration near a diamond grain must be decreased, and the strength properties of the binding matrix phase (a WC-Co hard alloy) must be increased. The required complex of characteristics can be obtained by using shock waves in preparation of diamond - hard alloy materials. In this work, the shock compressibility of powder mixtures diamond - VK6 hard alloy and diamond - VK20 hard alloy were studied by the familiar reflection method. For all pressures applied, in curves of the dependences D(U), no bends were observed, which indicates the absence of direct and reverse phase transformations both in the components of the hard alloy and diamond. This is a positive factor from the viewpoint of retention of the diamond modification of carbon in the shock-compressed material and determines the appropriate range of the shock-wave effect. The structures of the hard alloy matrices of diamond-containing materials sintered in shock waves and by traditional methods are considered. It is shown that the hard alloy sintered in shock waves is an appropriate matrix for diamond-containing materials. In this case, no mass loss of the diamond micropowder as a result of its interaction with the matrix material is noted, and up to 90 % of diamond grains remain undamaged. Under the action of the high pressure of shock compression, the modulus of elasticity, compression strength, and wear resistance of the composite diamond - hard alloy material increase. The composites obtained can be recommended as wear resistant elements of highly loaded friction pairs operating in an abrasive medium with a high level of contact stresses.

SYNTHESIS OF FULLERIDS IN A DISPERSION POROUS METAL MATRiX

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The conditions of transformation of carbon in its super-hard forms (diamond, fulleren) assume extreme methods with external application of super high pressure and temperatures. The known methods are unproductive; therefore a perspective is the study of "internal" reserves of metal matrixes for synthesis of carbon phases during the sintering stage of steel resulting in the creation of composite materials. Such an opportunity is realized in a dispersion-porous material during solid sintering at relatively low temperatures. The formation metal fullerids in a steel matrix with the porosity of 17 % and pore sizes less than 5 microns made on a basis of mechanically alloyed powders is revealed. Presumably, the conditions for synthesis of metal fullerids are created by high pressure in dispersed porous powders, including much deformation of the crystal lattice of graphite and creating (in view of the small size of Young's module) a deformation of about a hundredth percent, and also pressure during changes of volumes during phase transformations of the matrix. The composite material containing metal fullerids, is applied to produce wear-resisting parts.

A NEW COMPOSITE MATERIAL WITH A HIGHER DAMPING ABILITY OBTAINED UNDER HIGH PRESSURE

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A new composite material with higher damping ability has been produced from metallic Ni and Ti-powders under high-pressure conditions with use of a specialized technology. The damping ability for the produced composite material is several orders of magnitude higher compared to its analogue alloy. Application of vibration-damping elements made of produced titanium nickelide in cutting and

drilling tools proved the effective damping of the vibrations arising under permanent load, impact and impact-rotation resulting in a considerable increase of wear resistance of cutting tools and diamond drill bits.

A BASALT COMPOUND CERAMIC COMPOSITE REALIZED BY SINTERING

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Basaltic-andezite type volcanic rocks from region Malnas - Bixad - Tusnad (Harghita Mountains, Romania), with the mineralogical composition 40 - 45 % felspar-plagioclase, 45 - 50 % piroxen, 2 - 4 % olivine, 5 - 8 % opaque minerals, 3 - 4 % isotropic glass and oxide composition of 56.5 % SiO_2; 16.5 % Al_2O_3; 5.5 % Fe_2O_3; 6.8 % CaO; 4 % MgO; 3.7 % Na_2O; 3.4 % K_2O can serve as ceramic raw material, being a complex alkali - alkali earth silicate zone labrador - andezine from albit - orthoclase - anortit system, with a complet melting at 1270°C. In a ceramic mass containing basaltic-andezite, porcelain clay and alumina, basaltic-andezite is a basic component. The elaborated ceramic material, with a high durability, sintered at 1350°C, has properties of a superior quality in comparison with electrical engineering porcelain (CER 110, CER 111), especially in mechanical properties: bending and compression strength, friction resistance, resistance to chemical agents. It's electrical and thermal properties are also remarkable. The main properties which determine the utilization possibilities of the elaborated ceramic material, are: apparent density (2.4 g/cm^3), porosity (0.1 %), bending strength (90 MPa), compression strength (250 MPa), electric resistivity at 20°C ($5 \cdot 10^{11}$ ohmm), dielectric strength (9 kV/mm), relative permittivity (6), thermal dilatation coefficient, 20 - 600°C ($4 \cdot 510^{-6}$ K^{-1}), thermal shock resistance (200 K), Mohs hardness (7), resistance to abrasion (0.25 g/cm^3) and resistance to chemical agents (98 %). The experimented basaltic-andezite compound ceramic material has good mechanical, electrical and thermal properties and can be recommended for electrical-insulator products at low voltage, pieces for machine construction resistant to abrasion and corrosive surroundings, packing rings, bushes, plate tiles, etc.

EFFECT OF DIFFERENT ADDITIVES ON LIQUID-PHASE SINTERING OF ALUMINA CERAMICS

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Low temperature sintering can be achieved through a selected range of additives, which promote liquid-phase formation. These components usually affect the properties promoting decrease in toughness and thermal shock resistance. In this work, additions of MnO and TiO_2 were employed as a means of lowering the sintering temperature of alumina ceramics. Effects of sintering additives used were evaluated through measurements of fracture toughness, work of fracture and thermal shock curves. The presence of a liquid phase during sintering is deleterious to the toughness and mechanical strength. High densification levels were obtained at temperatures of approximately 1300°C, with no observable detrimental effect on the thermal shock behavior. The combination of TiO_2 and MnO can improve alumina densification due to the formation of a low viscosity liquid at the sintering temperatures. This enhances the diffusion rates and can significantly reduce the sintering temperatures.

SYNTHESIS OF "IN SITU" REINFORCED Si_3N_4 COMPOSITES

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Composite materials on the basis of β-Si_3N_4 were synthesized by introducing previously prepared β-Si_3N_4 seeds, into the mixture of α-Si_3N_4 (LC12 SX-Starck) with an additive. The procedure for seed preparation was described in detail. Two additives were used for sintering of composites: a mixture of Y_2O_3 - Al_2O_3, and CeO_2, in the amount of 10 mass%. Homogenization of seeds and the starting mixture was performed in an attritor. Green pellets were obtained by prepressing and thereafter by isostatic pressing under the pressure of 350 MPa.

Sintering of green pellets was performed at 1800°C, for 1, 2, 4 and 6 hours, in flowing nitrogen. The powder bed technique was used to prevent thermal decomposition of Si_3N_4. Characterization of sintered samples involved density measurement by the Archimedes method, phase analysis by X-ray diffraction, and microstructural analysis by SEM. The obtained results enabled the discussion of densification process development as a function of additive type, sintering time, and seeds concentration. Moreover, micrsostructural changes were followed, as well. Finally, hardness and fracture toughness were measured. The obtained results showed that the densification degree dependence on the type of additive was stronger in comparison with the dependence on the sintering time. The densification degree was also dependent on the seed concentration. A bimodal microstructure was observed with samples containing β-Si_3N_4 seeds. The microstructure differed with different additives. The dependence of properties of composites was also followed as a function of the soaking time, type of additive and seed concentration.

HOT PRESING OF SEEDED Si_3N_4 BASED COMPOSITES

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Reinforced SiN composites were obtained by introducing β-SiN seeds into the α-SiN matrix. β-SiN seeds were obtained from the mixture of Y_2O_3, SiO_2 and Soil, which was heated at 1850°C, for 6 hours in flowing nitrogen. The preparation of seeds from these samples was described. Two types of additives were used as densification aids: Y_2O_3-Al_2O_3 mixture, as well as Y_2O_3 in the quantity of 10 mass%. Homogenization of seeds and the previously prepared mixture with additives (in a vibro mill) was performed in an attractor in isopropanol, for 6 hours. The concentration of seeds in the mixture varied from 1-5 mass%. The obtained powders were dried and sieved before hot pressing. Hot pressing was performed at 1700-1750°C, under the pressure 48 MPa, in flowing nitrogen. The isothermal heating time ranged from 1-6 hours. The densification degree, during hot pressing, according to our results, was affected by the additive type and seed concentration.

The isothermal heating time did not affect the density change to a great extent. The microstructure, however, was affected both by the isothermal heating time and by the type of the liquid phase. The phases present were detected by X-ray analysis, and hardness and fracture toughness were determined by the indentation method. These results will be discussed, as well.

CONSOLIDATION OF A POWDER MATERIAL IN CONDITIONS OF THE COMBINED INFLUENCE OF DIFFERENT TECHNOLOGICAL FACTORS

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The sintering concept includes, first of all, a variation of pore characteristics. This concept must also include numerous effects on interparticle surfaces. Simultaneously one can observe changes of the chemical composition and material modular state. Processes proceeding in conditions of intensive thermo-mechanical influence on the treated material are especially specific. In this paper, problems connected with the formation of a powder material and its surface layers in conditions of chemical thermal treatment and impregnation with a melt, combined with the use of mechanical loads, are examined. New results of the liquid phase influence on compaction of powder preforms, subjected to impregnation, are obtained. The presence of a liquid phase in preform surface layers can be also connected with the change of the material chemical composition as the result of boronizing, siliconizing or other kinds of chemical thermal treatment.

INFLUENCE OF DEFORMATION DEGREES ON THE ANNEAL HARDENING EFFECT IN SINTERED COPPER ALLOYS

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The strength properties of cold-worked substitional solid solutions are increased upon annealing up to the recrystallization temperature in several alloy systems. This effect is termed *anneal hardening* and is mainly applied to copper alloys when producing spring materials for electro-mechanical devices. Materials subjected to investigations were prepared by a powder metallurgical method. Copper and copper alloys, CuZn4 mass% and CuNi5Sn2 mass%, were prepared using electrolytic copper powder and powders of alloying elements. The pressed compacts were sintered isothermally at 850°C. After that, sintered copper and copper alloys were subjected to cold rolling with different degrees of deformation (30, 50 and 70%). Copper and copper alloys in the cold-rolled state were investigated (hardness, electrical conductivity). After that, samples of alloys in the cold-rolled state were isochronally and isothermally annealed up to the recrystallization temperature during which hardness and electrical conductivity were measured. These investigations show that the *anneal hardening effect* occurs in alloys in a temperature range of 180 – 400°C, followed with an increase in hardness. The hardness values increased remarkably for all applied deformation degrees, i.e. 30, 50 and 70 %, but it is most expresive for 70 % of deformation.

DISTRIBUTION OF SiC PARTICLES IN THE ALUMINIUM MATRIX COMPOSITE - CW67

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One of the most important phases in the production of DRA (Discontinuous Reinforced Aluminum) materials is improved uniformity of the reinforcement distribution. The objective of the present work was to study optimal conditions for uniform SiC particle distribution in the commercial Aluminium matrix alloy (CW67). SiC particle distribution was investigated by means of quantitative metallography. The results show that uniformity of SiC particle distributions generally depends on SiC particle size and volume fraction as well as the blending time. For the investigated volume fraction (5, 10 and 15) and particle size (0.7 and 15μm) of SiC, the best result is obtained for the volume fraction of 15 vol.% and particle size of 0.7 μm after 30 min of blending time.

THE IFLUENCE OF REOLOGICAL PROPERTIES OF GLASS ON THE STRUCTURE OF A THREE LAYER OPTICAL FIBER SINTERED BLOCK

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Sintered fiber-optic blocks are used as optical field flatters in lens systems. Besides strongly determined optical requirements, certain thermal and chemical properties exist which must be taken into account. They also have to be vacuum tight. For the production of these blocks, coherent bundles of three layer optical fibers (diameter below 10μm) were used. Each fiber in a coherent fiber optics element consist of a glass core clad with a jacket glass of a lower refractive index and with an absorbing layer of black glass for the prevention of cross talks between adjacent channels. Besides optical requirements, glasses for the production of coherent fiber optics bundles have to be reologocaly compatible and with adequate thermal expansion coefficients. In order to have the circular cross section of individual glass layers it is necessary, to have their viscosities as $\mu_1>\mu_2>\mu_3$, where the outer third glass layer has the lowest viscosity coefficient at a given temperature. Also it is necessary that thermal extension coefficients of glasses are close to each other $\alpha_1<\alpha_2<\alpha_3$. Using multifiber bundles as basic components for building blocks, manufacturing processes for fusing blocks involve requirements for optimum sintering conditions, usually a delicate balance of three parameters - time, temperature and pressure. During the process of sintering, even if optimal conditions are achived, sintering defects may occur, such as chicken wire, blemishes, pits and chips. The aim of this work is to present the differences in sintered block structures caused by different properties of glasses used for the core and cladding of a single fiber. Two types of fibers have been used for the experiments, a fiber with lead crystal core and a fiber with a lanthanum glass core. Both fibers had borosilicate glass cladding and an absorbing layer of black glass.

INCAPSULATION OF $BaTiO_3$ CERAMICS INTO A LDPE POLYMER MATRIX

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Ferroelectric composites of ceramics and polymer should attract considerable attention since their structure combines a high ferroelectric activity of ceramics and mechanical strength of polymers. Having this in mind, an investigation of the incapsulation of $BaTiO_3$ ceramics into LDPE polymer matrix has been performed. Different amounts of $BaTiO_3$ have been mixed in an extruder with low density polyethylene (LDPE) and compacted by hot pressing at 180°C and 1.75 MPa. Structural investigations of polymer composites were carried out, using SEM and XRD methods. A study of mechanical properties of the samples has been performed using stress-strain measurements.

NON-OHMIC BEHAVIOUR IN MECHANICALLY ACTIVATED ZINC OXIDE

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Zinc oxide is greatly used for the production of materials and components for different applications due to its specific properties. Thus, investigations of possible modifications of its properties are of both scientific and practical interest. The process of macro and microstructural transformation of zinc oxide powders, which were mechanically activated by grinding in a vibro-mill was investigated on the dependence of electrical properties. Since the grain size and porosity are major terms for the quantitative analysis of microstructure, we have followed electrical properties (I-V), densification and grain growth during sintering of mechanically activated zinc oxide. It was shown that mechanical activation contributes to a gradual modification of the microstructure and fine defect structure of zinc oxide powders and finally of electrical properties, since non-ohmic behavior was observed in mechanically activated ZnO without key compounds such as Bi_2O_3.

INFLUENCE OF DOPING ON THE ELECTRICAL PROPERTIES OF BARIUM TITANATE - BASED CERAMICS

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$BaTiO_3$ is the most studied material and is intensively used in applications such as a high dielectric constant in MLCC, piezoelectric transducer and PTCR materials. The addition of small amounts of dopants in A, B or in both A and B sites of the perovskite cell ABO_3 of barium titanate cause a change in the microstructure and also in the final properties of the sintered material, so that the requested properties for applications can be modulated using appropriate dopants in convenient concentrations. In the present work the influence of dopants both in the case of insulating and semiconductor $BaTiO_3$ – based ceramics are analyzed. The addition of isovalent ions such as Sr^{2+} on Ba^{2+} sites and Hf^{4+}, Zr^{4+} in the Ti^{4+} positions of a $BaTiO_3$ perovskite cell act as shifters of the Curie temperature and

increase the dielectric constants and the relaxor behavior and improve the aging properties, by comparison with the undoped $BaTiO_3$ ceramic material. The role of n-doping (La^{3+}, Er^{3+} dopants on the Ba^{2+} site with electron compensation) on the microstructure, the semiconducting and Positive Temperature Coefficient of Resistivity (PTCR) properties of $BaTiO_3$ have also been analyzed. Optimum doping parameters have been found in order to obtain low resistivity at room temperature and 3 - 5 order jump of the resistivity (PTCR effect) at the transition temperature.

THE INFLUENCE OF ALLOYING ELEMENTS ON THERMAL STABILITY AND CRYSTALLISATION PROCESSES OF MULTICOMPONENT AMORHOUS ALLOYS

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The composition of amorphous alloys, technological methods for obtaining these alloys and consequent heat treatment determine the thermal stability and physical properties of these objects. One of the directions in searching for an optimum composition of amorphous alloys, with the purpose of extension of the temperature interval of thermal stability by suppression of the phase-formation of crystalline phases process, is a choice of a system of the amorphous alloy FeB eutectic composition with consequent addition of high-temperature alloying elements (Mn, Co, Ni, Nb, Mo, Si) in a quality of the "basis". The crystallisation processes of four amorphous alloys $Fe_{70}Mo_{10}Si_6B_{14}$, $Fe_{76.5}B_{14}Mn_2Mo_2Co_2Nb_{0.5}N_1$, $Fe_{14}B_{14}Si_2Nb_2Co_2Ni_4Mo_2$, $Fe_{78}B_{14}Si_2Nb_{0.5}Mo_{4.5}Ni_1$ during continuous heating to the temperature of full crystallisation and at long-term isothermal annealing were investigated. The "basis"-system for these amorphous alloys was $Fe_{100-x}B_{14}$ ($X = 14\text{at.}\%B + \sum_i X_i$, where $\sum_i X_i$ - is the sum of concentrations of alloying elements). For the basis systems the relative integrated Gibbs free energies in amorphous and crystalline phases are constructed, the work of formation of the new phase nuclei is calculated, the temperature intervals of formation and growth of the crystalline phases and thermal stability are defined. The dependence of the

volumetric part of the crystalline phase on the temperature and time isothermal annealing is calculated for multicomponent amorphous alloys on the base of experimental research of the relative changes of volume $\Delta V/V$ during formation and growth of crystalline phases during continuous heat and isothermal annealing. The analysis of obtained results has allowed us to make the following conclusions: the importation of high-temperature alloying elements into "basis" systems expands the temperature interval of thermal stability approximately to 100 - 150 K and raises the crystallisation temperature for 100 K in comparison with "basis" systems; the crystallisation process in investigated alloys is multistage, at first the dominating phases form and grow, and after that small-dispersion crystalline phases form.

PROPERTIES OF SINTERED MATERIALS

DIELECTRIC CERAMICS FOR LTCC TECHNOLOGY

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The intensive competition between producers of electronic devices is forcing a rapid pace of further development of microwave wireless communication and information systems towards multi functional pocket- or credit-card-size devices. It also motivates the development of new systems and technologies, expansion of the marketplace and, especially important, the reduction of costs. Over the last ten years, the low-temperature co-firing ceramics (LTCC) technology has advanced to such an extent that it now allows the integration of a variety of passive components within the LTCC module. However, to achieve better performance some of them are still mounted as discrete components on the top of the module. The development is focused on Bi-rich compounds, where low sintering temperatures and high permittivities are expected. Among them, ceramics based on Bi_2O_3-TiO_2, Bi_2O_3-ZnO-Nb_2O_5 and Bi_2O_3-TeO_2 systems are most important. A material system consisting of low- and high-permittivity LTCC material was developed on the basis of Bi-eulytites ($\kappa' = 16$) and sillenite ($\kappa' = 40$) compounds. Ge- and Si-analogues of both structures meet the main requirements for the LTCC with respect to their sintering behavior ($T_s = 850 - 900°C$), mutual chemical compatibility and compatibility with silver electrode as well as dielectric properties. In the lecture, the synthesis, sintering behaviour and microstructural features of such ceramics will be discussed with respect to their mutual compatibility and resulting dielectric properties.

HIGH STRENGTH Al-Zn-Mg-Cu ALLOYS WITH Sc ADDITIONS

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The highest strength (up to 650 MPa) attained in commercial aluminum alloy products at room temperature is developed in Al-Zn-Mg-Cu alloys of the 7XXX series. Repeated attempts to further increase the strength of alloys of this system by increasing the content of the main alloying components (mainly Zn and Mg) have shown that ultimate strength can be increased slightly, but plasticity and the resistance to corrosion cracking fall below the levels acceptable for structural alloys. It has recently been shown that an addition of Sc may improve both strength and plasticity of aluminum alloys. Scandium in Al alloys may be used as a precipitation-strengthener, grain refiner and recrystallization inhibitor. The hardening effect from Sc is much higher than from any other alloying element. A small addition of Sc (~ 0.2 wt.%) increases the recrystallization temperature of Al-Zn-Mg alloys above the solution heat treatment temperatures. Stress corrosion resistance of Al-Zn-Mg alloys increases also in alloys with Sc additions. Combined alloying of Al alloys with Sc and Zr is even more effective. All these problems are discussed in the present talk as the "Sc effect" of improving mechanical properties in aluminum alloys. The investigation was carried out for Al-Zn-Mg-Cu alloys with additional alloying by Sc and Zr. Alloys were produced by PM and melting. Rapidly solidified aluminum alloy powders were produced by high-pressure water atomization of the melt. The powder compacts cold pressed to about 30 % porosity were subjected to hot vacuum degassing, hot forging at the same chamber and to hot extrusion to produce rods. Melted ingots of alloys were also extruded in order to produce rods. It was shown that in alloys containing Sc and Zr the concentration of Zn might be increased to 10 – 12 % that enables increase of UTS up to 800 MPa at a sufficient level of plasticity. It was also shown that effectiveness of Sc additions is higher for melted alloys than for PM alloys, because a highly dispersed structure and high recrystallization temperature are achieved in the latter due to a high cooling rate. But the PM process, in which the rapidly solidified powders are used, enables improvement of mechanical properties of Al-Zn-Mg-Cu alloys without costly Sc additions.

INTERFACE DESIGN OF HIGH COERCIVE SINTERED PERMANENT MAGNETS OF THE $SmCo_5$ - TYPE

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The sintered permanent magnets (SPM) based on powders of rare earth metals are non-equilibrium multiphase systems. The processes of structure self-organization giving rise to special crystallographic and magnetic textures are characteristic of these systems. Excellent magnetic properties of SPM can be obtained by improving strong requirements on the grain and interface structure. The influence of interface structure, boundary secondary phase distribution and chemical composition on the magnetic properties of SPM based on $SmCo_5$ high dispersion powder is investigated. The phenomenon of high coercivity of $SmCo_5$ magnets has been treated in the framework of the theory of interfaces (calculations of the crystallographic parameters and atomic models of special coherent grain and phase boundaries in the Sm-Co system), which affords some new insight in its origin. The texture analysis and precipitation processes of secondary phases on grain boundaries are compared with interface crystallography. The model calculation based on bicomponent phase diagram and composition correction with oxygen content and magnet density is proposed.

The experimental observations revealed:

- the influence of external magnetic field during powder consolidation process on the shrinkage and interface pore distribution;
- the simultaneous increase in the rate of shrinkage and coercivity, as the Sm content in the alloy exceeds its stoichiometric amount in the $SmCo_5$ phase;
- the definite crystallographic orientation of the secondary Sm_2Co_7 and Sm_2Co_{17} phases, as interface precipitates and their influence on coercivity;
- the role of magnetocrystalline anisotropy and interface atomic structure in domain wall - grain boundary interactions, pinning and reverse domain nucleation mechanism in $SmCo_5$ magnets with one [0001] easy magnetisation direction.

PHOTOACOUSTIC INVESTIGATION OF SINTERED MATERIALS

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Photoacoustic (PA) and photothermal (PT) science and technology extensively developed new methods for the investigation of various materials during the last ten years [1-2]. The PA and PT techniques were recently established as a diagnostic method with good sensitivity to thermophysic parameters. It is very important to point out the connection between PA and PT science and material science. The excited temperature oscillations in materials - the thermal waves, generated by the absorbed intensity-modulated energy beam, can play a dominant role in PA and PT signal generation. The excited beam generates depth-dependent thermal waves, which contribute to the generation of elastic waves. The time periodic generation of heat and mechanical vibrations, i.e., thermal and elastic waves can be manifested in various ways. One is a sound generation (the PA effect), or an optical probe beam deflection (the PT deflection), or an infrared emission (the PT radiation), etc. The general theoretical analysis of PT and PA effects consists of modeling a complex system by simultaneous analysis of the coupled thermal and elastic transport equations. This theoretical treatment enables quantitative accounts of the amplitude and phase of the PT or PA signal and describes these functional dependencies on modulation frequency, thermal and other physical properties of the material. It is well known that the main parameters of sintered materials are defined by their microstructure. The propagation of thermal waves in solids is strongly influenced by the material's microscopic properties, by its physical microstructure, and especially by the distribution of inner interfaces. Inner interfaces limit the free path length of carriers in a solid such as electrons or phonons and therefore reduce the thermal conductivity. The correlation between microstructure and local thermal properties such as thermal diffusivity in a solid, and the fact that the penetration depth of thermal waves in a periodically illuminated sample can be controlled by the modulating frequency, makes it possible to establish a nondestructive technique for measurement of thermophysical parameters. In this report the thermophysical properties of sintered materials were investigated using

the PA method. The PA amplitude and phase signals as a function of wavelength of incident beam or modulating frequency, for various sample thicknesses, were measured and analysed. Sintered materials give a large PA signal, but their interpretation in terms of thermal quantities is not as easy as for homogenous samples. Obtained data show the presence of thermal wave dispersion within the sample, i.e. the thermal properties are affected by the random geometry - fractal structure of such a sample. When the frequency-dependent PA is applied to sintered materials, the amplitude and phase PA signal shows a frequency dependence, which significantly deviate from the behaviour of a compact homogenous sample [3]. The thermophysical properties are affected by the random geometry of such a sample. A relationship between the PA signal and the porosity of sintered materials has also been established by using the theory of fractals.

1. D. Almond, P. Patel, Photothermal Science and Techniques, Chapman & Hall, London, 1996.
2. A. Mandelis and K.H. Michaelian, Eds., Photoacoustic and Photothermal Science and Engineering, Special Section of Opt. Eng., **36** (2) 1997.
3. D.M. Todorović, P.M. Nikolić, D.G. Vasiljević-Radović, A.I. Bojičić, Recent Trends in Science and Technology of Sintering – Book of Abstracts, IX Word Round Table Conference on Sintering, Eds. M.M. Ristić & M.V. Nikolić, Beograd, 1998, p. 59.

MAGNETO IMPEDANCE EFFECT IN JOULE-HEATED Fe-Al-Ga-P-C-B METALLIC GLASSES WITH A LARGE SUPERCOOLED LIQUID REGION

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Amorphous Fe-(Al,Ga)-(P,C,B,Si) systems have very promising soft magnetic properties for various technical purposes. The most useful practical applications are magnetic field and current sensors based on the magneto-impedance effect. In this study we present the optimization of the longitudinal

magneto-impedance (MI) response in melt-spun $Fe_{72}Al_5Ga_2P_{11}C_6B_4$ ribbons annealed by dc Joule-heating. Evolution towards the optimum annealed state was studied by means of X-ray diffraction (XRD), electrical resistivity, hysteresis and MI measurements. The thermal stability of the prepared ribbons was examined by a differential scanning calorimeter (DSC). The Curie temperature (T_C), glass transition temperature (T_g), and supercooled liquid region ($\Delta T_X = T_X - T_g$) observed from the DSC trace are 574, 736 and 65 K, respectively. The structure of as-cast samples is composed of a glassy matrix without any crystalline phase. Annealing was carried out in multi-step heat treatments for 40 seconds with successive increase of maximum applied heating power (P_S) in the range from 2 to 5 W/cm^2. XRD patterns indicate crystallization after applying P_S over 4.7 W/cm^2. The samples were magnetically characterized using a quasi-static B-H loop tracer. Thermal treatment leads to progressive magnetic softening associated with structural and stress relaxation. Decreasing of coercivity (H_C), i.e. increasing of permeability is necessary for improvement of the MI response. The lowest coercivity of 2.14 A/m was found for samples heated with P_S of about 3.25 W/cm^2. Due to induced transverse magnetic anisotropy resulting from the magnetic field created by the annealing current, Joule-heating favors a significant change in magnetic anisotropies introduced during the ribbon preparation. The presence of the transverse magnetic anisotropy is a dominant feature for improvement of the MI response in a planar conductor (i.e. ribbon form sample). The MI effect has been explored on as-cast and current annealed samples in the 10 kHz - 10 MHz frequency range using an oscilloscope to monitoring the output voltage in a four-point probe technique. The MI ratio defined as $\Delta Z/Z = (Z(H) - Z(H_{max})) / Z(H_{max})$ is dependent on frequency (f) as well as on the external static magnetic field intensity (H). For all samples, the MI ratio first increases with frequency and reaches maximum at about 1.6 - 2 MHz, then decreases with further increase of frequency. The best MI ratio was found to be of about 25 % (at f = 2 MHz for applied external magnetic field of H_{max} = 5.6 kA/m) and sensitivity of 9 %/kA/m in a low field region has been attained after applying P_S of about 4.7 W/cm^2.

ELECTRON STRUCTURE, PROPERTIES AND X-RAY SPECTRA OF NEW SINTERED INTERMETALLIC COMPOUNDS

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The most wide spread among rare earth intermetallic compounds R.E.—M—X systems (M — transition 3d-elements; X – Si, P, Ga, In) are compounds of the $CeGa_2Al_2$ structural type, which in fact is a superstructure of $BaAl_4$. The R.E. atoms occupy positions of Ba atoms; M and X atoms regularly occupy two positions of Al atoms. As a result, the atoms of each element in the structure are surrounded preferably by the atoms of other elements. Samples with phosphorus were prepared by the sintering method, for the same time as other compounds - by direct arc melting of pure components. In recent years there has been a continually increasing interest in investigation of ternary compounds, where R.E. — Ce or Yb, which have a large variety of ground state properties. Heavy fermion superconductivity and band magnetism, as well as a special class of heavy fermion systems with non-Fermi liquid behavior in their basic properties have been observed in compounds of this type. We investigated magnetic properties of comparatively new compounds CeM_2P_2 (Fe, Co, Ni), CeMP, $YbNi_4In$ and $CeNi_4In$ with valence unstable Yb and Ce. Our experimental L_{III} - absorption spectra of Ce and Yb were obtained at 78 and 300 K. X-ray emission spectra R, M and X atoms in RM_2X_2 compounds have been investigated and the density of total and partial electron states in these phases have been calculated within the self-consistent LMTO method. Effective filling numbers of electrons in different bands of components in RM_2X_2 have been calculated.

ac IMPEDANCE SPECTROSCOPY OF SnO_2 BASED CERAMICS: OPTIMIZATION OF MEASURING CONDITIONS

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ac impedance spectroscopy was applied to investigate electrical properties of the grain boundaries in SnO_2 ceramics doped with CoO, Cr_2O_3 or Nb_2O_5. It was found that grain boundary response is strongly influenced by electrical measurement conditions, such as type of electrode, atmosphere and temperature. These parameters were optimized to separate different processes that can take place at grain boundaries, as well as to reduce the influence of porosity and gas sensitivity during measurements. The best results and the most reliable data could be obtained with sputtered Au electrodes.

PROPERTIES OF DYNAMICALLY CONSOLIDATED COMPOSITE MATERIALS

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Industrial interest in composite materials has lead to an examination of the effect of shock waves on physical and mechanical properties of dynamically consolidated powders. Two copper powders were implosively compacted singly with graphite and one grade of polyvinyl chloride powders. Pressure generated ranged from 5 to 28 GPa for both composites. The effect of the original morphology, particle size, and composition on the final properties of a composite is presented. Compact density was shown to increase with compacting pressure up to

a definite limit and decreases with further increase in the pressure. Associated microstructure examination showed disappearance of interparticle bonding. The microhardness is increased with the induced pressure in the range investigated.

MONITORING THE THERMAL SHOCK BEHAVIOR OF ALUMINA BASED REFRACTORY BY SONINIC MEASURMENT

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Thermal stability of a refractory material with 28 % Al_2O_3 was investigated. The water quench test (JUS.B.D8.319.) was applied as the experimental method for thermal stability testing. The dynamic Young modulus of elasticity was calculated using measured values of longitudinal (Vp) and transverzal (Vs) velocites. Values of the dynamic Young modulus and changes in the compresive strength during testing were presented as a function of the measured number of quench experiments. Changes of fracture resistance parameters caused by thermal shock were also presented. Analysis of the thermal shock behavior of the samples based on the obtained results was given.

ADVANCED COMPOSITE MATERIALS OF THE AlN-SiC-TiB_2 SYSTEM, THEIR STRUCTURE AND PROPERTIES

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Development of heat-resistant composite ceramics with a high level of physical-mechanical properties (hardness, bending strength, toughness coefficient) as well as tribological characteristics (friction coefficient under high slipping velocities and loads) corresponding to the demands of contemporary industry is

one of the important problems of up-to-date materials science. For the manufacturing of monolithic composite materials the following processes can be used:

1. Pressing with a plastificator with further sintering in high-temperature furnaces in vacuum or a protective medium (argon, nitrogen, helium, hydrogen etc.);
2. Pressing under pressure (hot pressing) in graphite moulds;
3. Isostatic hot pressing in special ampoules in a protective atmosphere.

In this study the 1st and 3rd technological methods were used for manufacturing new composite materials. Hot pressing was implemented in graphite moulds, in which the inner surface was covered with boron nitride. The powders of aluminium nitride, silicon carbide and titanium boride were mixed and simultaneously ground in a drum lined with aluminium nitride in a planetary mill in the acetone medium during 6 - 8 h. For the study of sintering and determination of optimum process parameters (temperature, time, pressure) the compacting kinetics were investigated for different temperatures and pressures. It was established that for the composite materials chosen the sintering temperature region was 1860-1890°C, the pressure being 150 - 180 MPa, the sintering time being 10 - 25 min, in dependence on the demanded size of samples. The residual porosity of samples did not exceed 1 - 1.5 %. For the materials of the AlN-SiC-TiB_2 system the amount of second phases varied in the limits: SiC – 20 - 28 mass%, TiB_2 – 1.5 - 10 mass%. It must be noted that with an increase of titanium diboride content the structure of the composite became a fine-dispersion one, i.e. the presence of TiB_2 prevented growth of aluminium nitride grains. According to EPMA data, the composites of this system had a heterogeneous structure with AlN as a main phase, the SiC and TiB_2 phases being uniformly placed along grain boundaries. For a study of physical-mechanical and corrosion properties of composite materials developed the corresponding compact samples were prepared. They were treated and annealed at temperatures of 1000-1200°C in vacuum during 15-20 h in order to take away the strains and homogenize the structure. Resulting from the complex study of physical-mechanical (strength) and tribological properties, a perspective of their application as high-performance materials has been shown. The measured values of hardness, bending strength and toughness coefficient in the case of small amounts of titanium boride additives are equal to: H_V = 21 GPa, σ_{bend} = 580 MPa, K_{1c} = 8.5 $MPam^{1/2}$. The friction coefficient

magnitude f = 0.36 - 0.21 under slipping velocity v = 16 m/s and load P = 5 MPa. Resulting from high-temperature corrosion tests up to 1600°C in air, it has been shown that composites of the AlN-SiC-TiB_2 system have an exceptionally high heat-resistance. The heterogeneous oxide film formed on the sample surface is characterized by extremely high adhesion in relation to the material substrate and fulfills the protective functions. The composite ceramics developed may be recommended as high-performance materials as well as targets for deposition of wear- and corrosion- resistant coatings.

MANUFACTURING, STRUCTURE AND PROPERTIES OF (TiCN-AlN)-(Fe-Cr) COMPOSITE MATERIAL

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Titanium carbonitride-based composites with aluminum nitride additives are perspective high-performance materials. AlN additives into TiCN enable significant increase of the heat-resistance of material. They essentially improve its tribologic characteristics. In this study ~20 % AlN was introduced into the TiCN composition. For the development of the (TiCN-AlN)-based composite it was necessary to choose the metallic binder. Therefore the mechanism of interface interaction in the (TiCN-AlN)-(Fe-Cr) system was investigated using the "sessile drop" method. The (TiCN-AlN) samples were wetted with Fe-Cr alloys in the concentration range of 5 – 25 mass% Cr. For all the alloys studied the formation of zero contact angles took place, the duration of their establishment being 3 – 6 min. This enables recommendation of Fe-Cr metallic binders for use in the development of wear-resistant ceramic-metallic materials on the base of (TiCN-AlN). The (TiCN-AlN)-(Fe-Cr) samples were manufactured by the hot pressing method in graphite moulds. It was established with the aid of XRD, metallographic and SEM methods that the following phases were found in the (TiCN-AlN)-(Fe-Cr) material: 1) titanium carbonitride as the main phase of a light-grey color with H_μ = 22.9 GPa; 2) a grey phase of aluminum nitride with H_μ = 13.9 GPa; 3) a white phase of aluminum; 4) a Fe-Al-based phase as the thin layers of metal between particles of the main phase, as well as some dark regions as Fe-Cr alloy layers

between grains and conglomerates of the main phase. According to results of EPMA, there is not more than 1 % Al in the main phase (TiCN), obviously, as the solid solution. The dispersion of structure, on the whole, is determined by the dispersion state of the TiCN main phase, for which the average grain size is equal to ~ 22.5 μm. The mechanical and service characteristics of the material obtained are the following: bending strength is 780 – 850 MPa, toughness coefficient is 8 – 9 $MPam^{1/2}$, hardness is 87 – 89 HRA, friction coefficient is 0.22 – 0.24, the temperature of oxidation start is 1300°C. The study carried out enables conclusion on the perspective of using the new composite material proposed as a high-performance material capable of working efficiently under conditions of high temperatures and intensive wear.

DEVELOPMENT OF ADVANCED TiCN-BASED COMPOSITE MATERIALS FOR FINE-DISPERSION WEAR-RESISTANT COATINGS

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Nowadays the commercial and research interest is directed to the development of composite ceramics and coatings. In these systems the modification of structure as well as choice of phase components enable the construction of a material/coating in such a way to combine the properties necessary for the tribological contact. In this study the investigation of structure, composition and tribological properties of both composite materials (CM) and coatings based on $TiC_{0.5}N_{0.5}$ with heat-resistant SiC, AlN additives and Fe(Ni)-Cr binder, developed in the IPMS of Ukrainian NAS, were generalized and discussed. The CMs were manufactured using hot press sintering as electrodes and powders being applied in the formation of electric-spark and gas-thermal coatings. The TiCN-AlN-based CM developed had the friction coefficient of 0.1 and wear intensity of not higher than 3.2 μm/km under high sliding velocity (15m/s) and the load of 10 MPa. The detonation and electric-spark coatings using TiCN-based CM ensured lower triboparameters compared with tungsten hard alloys coatings. The

results obtained were discussed from the point of view of physical-chemical interactions taking place at the tribological contact. The formation during tribooxidation of secondary films, consisting of the oxide phases forming solid solutions (TiO_2-Al_2O_3, Al_2O_3-SiO_2) and adhesionally strongly bonded with the CM/coating surface, promotes a decrease of wear and friction in the contact zone. The CM/coatings developed were recommended for applications under extreme exploitation conditions.

APPLICATION OF AN EXTERNAL MAGNETIC FIELD TO CONTROL THE GRAIN BOUNDARY MICROSTRUCTURE AND PROPERTIES OF $SmCo_5$, $Nd_2Fe_{14}B$ – MAGNETS

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The influence of crystal texturing, interface structure and secondary phase precipitation on the magnetic properties of permanent magnets of the $SmCo_5$ and $Nd_2Fe_{14}B$–type, obtained by sintering and melt spun – methods are investigated. The application of an external magnetic field of definite orientation during the material consolidation process changes interface pore distribution, magnet density and type of texture formation. Experimental data are discussed in terms of (1) generalised theory of interfaces and interfacial defect symmetry; (2) resonance principle of external field interactions and internal interface structure properties of the Sm-Co, Nd-Fe-B systems, arising from the self-organization process. The application of external field gradients is a powerful tool of boundary engineering to produce high-tech permanent magnets, based on ultradisperse $SmCo_5$ and $Nd_2Fe_{14}B$ powders with one easy magnetisation direction.

EFFECT OF POWDER PREPARATION AND SINTERING PROCEDURE ON THE MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF PLZT CERAMICS

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PLZT ceramics belongs to one of the very important groups of functional materials that represent the basis for the production of a large range of electronic devices. The structure and properties of ceramics depend on the powder preparation and thermal processing conditions. Variuos techniques have been used to obtain a chemically homogeneous and fine starting powder. The PLZT powder was prepared by two different production routes: the modified Pechini method, using the polymeric precursor method (PMM) and the partial oxalate method. A two step sintering process, including hot pressing, was carried out at 1100 and 1200°C. Phases obtained during the sintering process were investigated by SEM and EDS tehniques and dielectric properties such as permitivity and dielectric loss were measured in a frequency range from 1 kHz to 13 MHz. A significant difference in microstructural characteristics and dielectric properties, depending on powder origin and sintering procedure, have been noticed.

PROFILED CERAMIC MICROPACKAGES FOR MICROWAVE TRANZISTORS

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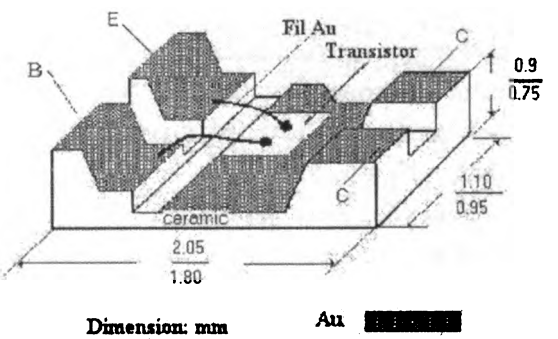
The present paper refers to realisation of profiled ceramic micropackages. Profiled ceramic micropackages (leadless inverted devices) are discontinuous

metallized ceramic elements, used to encapsulate some types of low power microwave diodes. Profiled ceramic micropackages, with parasitic capacitance's (0.1 pF) are manufactured using an original technology based on the injection of a 99 % α-alumina ceramic. The injection ceramic was realized by mixing together α-alumina powder with some additives at a temperature of 80 – 90°C. After homogenisation, the ceramic is transferred to the tank of injection equipment. The ceramic quantity is injected into a several hallowed metallic mould at a pressure of about 6 atmospheres. After cooling, the profiled ceramic elements are taken out from the mould, with the profile according to the figure given below. When designing the injection mould, the material contractions during the sintering process were taken into account. The value of the final product contraction is computed depending on the ceramics composition, element shape and size and the sintering temperature. After the sintering process was performed, the profiled ceramic elements are controlled dimensionally, in point planarity and surface roughness. After repeated chemical cleaning, the profiled ceramic elements are metallised using the thin film technique. Within the same vacuum cycle a sandwich of three metallic films is deposited on the ceramic element tops and profiles. The first Ti metallic layer is about 1000 Å thick, strongly adherent to ceramics, the second one is a 1 μm thick Ni metallic layer playing the role of a metal barrier metal and finally, the third layer is a 3400 - 3500 Å thick gold conducting layer. At the lowest part of the ceramic profile the element metallisation is interrupted using a diamond disc equipped installation. This metallisation interruption leads to the realization of profiled ceramic micropackage electrodes.



Profiled ceramic micropackage for microwave transistor.

ELECTRICAL AND MECHANICAL PROPERTIES OF SOME HIGH-ALUMINA COMPOSITIONS OBTAINED BY THE CASTING PROCESS OF AQUEOUS SUSPENSIONS

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This work presents the chose material compositions, the manner of preparing and shaping of composites. The measurements of the mechanical resistance and electrical resistivities on cast samples by pouring in plaster moulds are presented comparatively with the same properties obtained on the mould samples by other proceedings.

ON THE SINTERING PROPERTIES OF NICKEL-ZINC FERRITE WITH COPPER SUBSTITUTION

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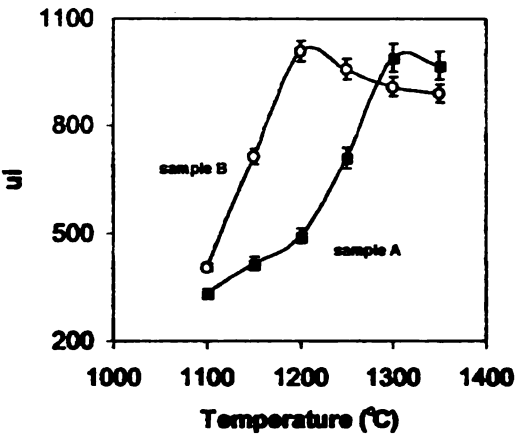
The recent applications of NiZn ferrites, such as multilayer chip inductors as well as suppressions of electromagnetic interference, commonly known as EMI, are working in notebook computers, hard disk drivers, pagers, cellular phones and other electronic products. New efforts have been done to achieve a reliable performance of NiZn ferrites for these applications. The present work is aimed at showing the influence of sintering conditions on the magnetic properties of some NiZn ferrites with chemical compositions: $Ni_{1-x-y}Zn_xCu_yFe_2O_4$, where: x = 0.65 and y = 0 (sample A); x = 0.65 and y = 0.20 (sample B). The samples were synthesized via the usual ceramic route. X-ray diffraction and Mössbauer spectroscopy measurements were used to provide information about the phase formation in the

NiZn ferrite powders presintered at different temperatures, in the range of 700 – 900°C. The green compacts were sintered in air, for 2 hours, in an electrically heated oven. The temperature was selected in the range from 1100 to 1350°C. Magnetic properties and microstructures of sintered bodies were investigated. It was found that NiZnCu ferrite bodies (sample B) sinter at lower temperature (with > 100°C) in comparison with NiZn ferrite bodies (sample A).



Variation of initial permeability (μ_i) versus temperature of sintering.

CORRELATION BETWEEN CHANGES OF THE THERMOELECTROMOTIVE FORCE AND ELECTRIC CONDUCTIVITY ON STRUCTURAL CHANGES OF THE $Co_{70}Fe_5Si_{10}B_{15}$ AMORPHOUS ALLOY DURING HEATING UP TO 600°C

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The crystallization process of the $Co_{70}Fe_5Si_{10}B_{15}$ amorphous alloy was investigated using measurements of the electric resistivity and thermo electromotive force in non-isothermal and isothermal conditions. It has been established that crystallization of this alloy occurs in two stages. The first

crystallization stage occurs in the temperature interval of 430 to 500°C, while the second stage occurs in the temperature interval of 520 to 570°C. It was shown that the thermo electromotive force coefficient stays constant up to 430°C and has the value of α_1 = 2.46 mV/°C by measuring the thermoelectromotive force of the thermocouple, obtained through coupling of the copper conductor and the $Co_{70}Fe_5Si_{10}B_{15}$ amorphous alloy. The thermo electromotive force coefficient was increased and has the value of α_2 = 3.43 mV/°C after crystallization of the amorphous part of the thermocouple. The density change of free electrons which occurs during alloy transition from amorphous to crystal state was determined from $\Delta\alpha = \alpha_2 - \alpha_1$ difference. Kinetic parameters for both stages of the crystallization process were determined using measurements of the electric resistivity change under isothermal conditions in the crystallization temperature region.

THE EFFECT OF TITANIUM CONTENTS ON THE STRUCTURE OF THE ALUMINIUM – COPPER – MAGNESIUM ALLOY

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In this paper, the effects of titanium contents in the interval of 0 – 0.25 % on the structure and properties of the aluminium – copper – magnesium alloy are examined. Formation of the Al_2Cu and Al_2CuMg compound are monitored using the X-ray powder diffraction method. By applying modern quantitative microstructure analysis based on QUANTIMET 500 MC equipment and the linear method of measurement of the effect of the quantity of titanium in the aluminium – copper – magnesium alloy has been monitored. Crystal lattice parameters, grain size, dendrite arm spacing (DAS), distribution of grain size, length eutectic (Le) and volume participation of α-hard solution and eutectic were determined. It has been noted that with the increase of the titanium content in the alloy, the mean value of the grain size decreases. Properties of these materials have also been examined including: hardness measurements and pressure strength determination.

1. L.F. Mondolfo, Aluminium Alloys: Structure and Properties, Butterworth and Co. Ltd, London, 1976, p.253.
2. X. Yang, J.D. Hunt and D.V. Edmonds, A quantitative study of grain structures in twin-roll cast aluminium alloys, part II: AA 3004, Aluminium, **69** (2) (1993) 158-162.
3. AM. Samuel, FH. Samuel, Effect of Alloying Elements and Dendrite Arm Spacing on the Microstructure and Hardness of an Al-Si-Cu-Mg-Fe-Mn (380), Journal of Materials Science, **7** (4) (1995) 1698-1708.
4. B. Radonjic, Directionality of Cast Aluminium Structure, Aluminium, **58** (11) (1982) 646-649.
5. W.Q. Jie, W. Reif, Effect of Cu Content on Grain – Refinement of an Al-Cu Alloy with AlTi6 and AlTi5B1 Refiners, Zeitschrift fur Metallkunde, **84** (7) (1993) 445-450.

INVESTIGATION OF THE STRUCTURAL TRANSFORMATION OF THE Cu - Al_2O_3 SYSTEM DURING SINTERING

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A study of the structural transformation of the Cu-Al_2O_3 system with 5, 10 and 15 % of a dispersoid was performed, by measuring the electric resistance, probe temperature dependence of specific electric resistance, such as the isothermal dependence of specific electric resistance on time. Measurement of the change of specific electric resistance in isothermal conditions at lower temperatures than the recovering temperatures, was used to determine kinetic parameters and energy of activation of the recovering process for samples pressed with 100 MPa. It was found that the recovery process in the temperature interval of 450 – 650 K, represents two processes. Experimental results indicate, that with an increase of the Al_2O_3 content the intensity of the change of electric resistance increases. Also, with an increase of Al_2O_3 content, for both stages, the constant of the process rate decreases, and the energy of activation increases.

STRUCTURAL AND MAGNETIC PROPERTIES OF Fe-BASED ALLOYS WITH A LARGE SUPERCOOLED LIQUID REGION PREPARED BY DIFFERENT RAPIDLY QUENCHING METHODS

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This paper presents the investigation of thermal stability, structural and magnetic properties of multicomponent $Fe_{62-x}Cu_xCo_8Ni_6Zr_8Nb_2B_{14}$ (x = 0, 0.5 and 1) alloys produced with melt spinning (ribbons) and suction casting (rods) methods. Thermal stability has been studied using differential scanning calorimetry and differential thermal analysis. Thermal behavior of all alloys exhibits a unique combination of a large endothermic supercooled liquid region followed by a wide exothermic single-step crystallization peak at higher temperature. The substitution of 0.5 at.% Fe by Cu causes an increase of the supercooled liquid region, i.e. temperature span between the onset temperature of the glass transition T_g and the onset temperature of crystallization T_X ($\Delta T_X = T_X - T_g$) is largest for x = 0.5 alloy (ΔT_X = 102 K). The reduced glass-transition temperature T_{rg} is about 0.54. Structural characterization was performed by X-ray diffraction. The structure of rod form samples is composed of a glassy matrix and metastable crystalline phase opposed to the completely amorphous structure obtained in ribbon form. The samples were 1-3 mm in diameter (rods) and about 50 mm thick (ribbons) and were magnetically characterized using vibrating sample magnetometry and a quasi-static B-H loop tracer. The saturation magnetization of this alloys is about 120 emu/g. Produced rods exhibit semi-hard magnetic properties with coercivity of about 70 Oe opposed to the soft magnetic properties obtained in ribbon form.

THE INFLUENCE OF $MnCO_3$ ON THE MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF $BaTiO_3$ CERAMICS

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The study of microstructural changes of $BaTiO_3$ ceramics, modified by a small content of $MnCO_3$ and their influence on dielectric properties has been performed. Microstructural investigations were carried out, using the SEM method and quantitative metallography methods. The grain size distribution and porosity of the samples were obtained. The linear intercept measurement method was used for estimating the grain size values and pore volume ratios. The results of capacitance and loss tangent as a function of different additive contents and samples densities were presented as well as the frequency characteristics of capacitance, loss tangent and impedance. It was noticed that the increase of initial densities of the samples decreases porosity of the samples, affecting grain growth and broadening the grain size distribution. Increasing of the additive concentration reduces the grain size of the samples, affecting the electrical properties of ceramics.

INVESTIGATION OF STRUCTURAL CHANGES OF THE $Co_{70}Fe_5Si_{10}B_{15}$ AMORPHOUS ALLOY BETWEEN ROOM TEMPERATURE AND 600°C

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Structural changes of the $Co_{70}Fe_5Si_{10}B_{15}$ amorphous alloy were investigated using measurements of the thermocouple thermo electromotive force between room temperature and 600°C. The thermocouple was obtained by coupling a copper conductor and the $Co_{70}Fe_5Si_{10}B_{15}$ amorphous alloy. It was established that the thermal coefficient of thermo electromotive force stays constant up to 430°C and has the value of α = 2.46 mV/°C. The thermo electromotive force coefficient was increased in the temperature region of 430 to 600°C. It was shown that the thermo electromotive force coefficient was constant in the whole temperature region between room temperature and 600°C and has the value of α_1 = 3.43 mV/°C after another annealing of the same thermocouple. The density change of free electrons in this alloy after crystallization was determined from the α and α_1 difference.

INVESTIGATION OF THE STRUCTURAL CHANGES OF PRESSED AMORPHOUS COBALT POWDER DURING HEATING BETWEEN ROOM TEMPERATURE TO 600°C

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The structural changes of pressed amorphous cobalt powder were investigated by measuring electric resistance and the relative change of magnetic permeability under non-isothermal and isothermal conditions. It was shown that the first thermal stabilization of the sample structure occurs in the temperature interval of 180 to 300°C. Powder crystallization occurs in the temperature interval of 450 to 570°C. The kinetics of the crystallization process was determined by measuring the isothermal time dependence of the electric resistance in the crystallization temperature region. It was noticed that the crystallization process takes place in two stages. The first crystallization stage occurs in the temperature interval of 450 to 500°C, while the second stage is in the temperature interval of 530 to 570°C. The temperature dependence of magnetic permeability was investigated up to 500°C. It was pointed out that the amorphous cobalt powder shows a stable structure in relation to magnetic properties up to 400°C.

THE METHODS FOR CHARACTERIZATION OF MAGNETIC PROPERTIES OF MELT – SPUN Nd-Fe-B ALLOYS

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The effect of the cooling rate and heat treatment on the coercitive mechanism and magnetic properties for defined initial chemical compositions of melt - spun Nd-Fe-B was investigated. The phase transformations as a function of the cooling rate and heat treatment regime are examined by determining the phase composition, by application of X-ray diffractometric analysis (XRD) and with Mössbauer spectroscopy phase analysis (MS). The temperature behavior aimed at selection of a favourable regime of heat treatment of the investigated rapid quenched alloys is examined by diffrential thermal analysis (DTA) with XRD. For determining the critical temperature of phase and magnetic transformations, thermomagnetic measurements (TM) were carried out on a vibratory sample magnetometer (VSM). Magnetic properties as a function of the examined parameters are measured at room temperature on the VSM with the magnetic field strength of 50 kOe. On the basis of the obtained experimental results the crystallization process as a function of the cooling rate and heat treatment regime was examined and studied, with the purpose of achieving optimal values of magnetic properties of the investigated melt-spun Nd-Fe-B alloys.

PROPERTIES OF THICK FILM NTC THERMISTOR LAYERS BASED ON A NANOMETRIC Mn, Co, Fe – OXIDE POWDER MIXTURE

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A NTC thermistor powder was formed of a MnO, CoO and Fe_2O_3 oxide mixture and ball milled to nanometric particle size (particles-clusters round 900 nm in average). After that the thermistor paste NTC 3K3 95/2 was composed of the same powder, 4 % of Bi_2O_3 and organic vehicle. NTC layers of different thicknesses were made by sequent ional screen printing and drying and then co-fired at 850°C/10 min in a hybrid conveyor furnace. Thick film microstructures were observed under optical and SEM microscopes. After that, the same samples were exposed to X-rays, when diffractograms were plotted and analyzed. The thermistor coefficient B, relation between thick film thermistor resistivity and geometry, and thermistor sensitivity were obtained from various planar thermistor geometries printed on alumina. At the end NTC thick film thermistor layers made on thin alumina and quartz substrate and thin discs (MLC – process) were exposed to a chopped laser beam in a photacoustic cell. Thermal diffusivity was calculated from the measured photoacoustic (PA) response. All the experiments done have been led by the intention to make new miscellaneous sensitive thick film planar NTC thermistors.

INVESTIGATION OF COLD SINTERED SE BY PHOTOACOUSTIC FREQUENCY TRANSMISSION

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Thermal properties of cold sintered Se powder were investigated using the photoacoustic (PA) method. The photoacoustic spectra as a function of modulating frequency of a laser beam for cold sintered Se were measured. The PA phase and amplitude measurements were used to obtain a diagram of thermal conductivity, which is attributed to the presence of a porous structure in the samples.

INVESTIGATION OF THE INFLUENCE OF WASTE MATERIALS ON THE PROPERTIES OF SINTERED ALUMO-SILICATE MATERIALS

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In this paper results obtained during an investigation of the properties of the proerties of sintered alumo-silicate materials with addition of waste materials, such as fly ash from electric power stations and powdered silicate glass, are presented. The influence of the pressing pressure in the pressure range from 15 to 35 MPa on physical properties of the materials before and after sintering have alos been examined. The results suggested that a significant difference in the properties of these materials exists.

EVOLUTION OF THE MICROSTRUCTURE

GRAIN SIZE EFFECT IN DOPED BARIUM TITANATE

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It is known that the dielectric properties of $BaTiO_3$ are dependent on its grain size. Coarse-grained ceramics of pure BT showed a lower dielectric constant at room temperature than fine-grained ones. Many authors considered that when the grain size is lower than 700 nm, the lattice of BT changes from tetragonal to pseudocubic, and the dielectric constant value is very low. In doped BT this effect is more complex, because it is necessary to also consider the influence of dopants. In the present case, the grain size effect on the structure and dielectric properties of donor-doped barium titanate was investigated. Nb^{5+}, Sb^{5+}, La^{3+} and Y^{3+} were used as dopants. Donor doped barium titanate was prepared from ceramic powders obtained by doping of commercial barium titanate, through the coprecipitation method and from an organometallic complex using citrates as precursors. The crystal and microstructure of sintered doped barium titanate were analysed. Dielectric properties were considered. The grain size effect was explained in the light of dopant distribution and differences in microstructure influenced by various routes for powder preparation. It was shown that the structure and properties were strongly dependent on the grain size of doped barium titanate.

DEPOSITION OF DENSE OXIDE FILMS BY A SPRAY PYROLYSIS TYPE PROCESS CALLED PYROSOL: INTERPLAY BETWEEN SOLUTION CHEMISTRY, GROWTH RATE AND FILM MORPHOLOGY

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Pyrosol is a chemical vapor deposition process (CVD), which can be applied to the deposition of dense ceramic-based films at low temperature [1-5]. Two of its major interests are that it operates at atmospheric pressure and it can be applied to deposition on a large area substrate. Usually, films are characterized with respect to their response to a given stimulus (light, gas, electric field or gas partial pressure for instance), but the science of the process is incomplete. This presentation is focused on the approach we have developed to answer one crucial question, which is the relation between the chemical nature of the precursor in the starting solution and the film morphology, especially the nature of crystal forms that grow during deposition. In this respect, we have used a theory of crystal growth called Periodic Bond Chain. The arguments will be developed on two systems, namely ZnO and SnO_2. In order to obtain high growth rates, it is preferable to have small and neutral complex molecules in the solution. With respect to film morphology, depending on the type of precursor, either equilibrium or non-equilibrium faces can develop. The effect of surfactants, which can segregate at the interfaces, on the growth of crystals will also be presented.

1. A. Smith, Thin Solid Films, **376** (2000) 47-55.
2. A. Smith, R. Rodriguez-Clemente, Thin Solid Films, **345** (1999) 192-196.
3. E. Dien, J.M. Laurent, A. Smith, J. Eur. Ceram. Soc., **19** (1999) 787-789.
4. A. Smith, J.M. Laurent, D.S. Smith, J.P. Bonnet, Thin Solid Films, **315** (1998) 17-21.
5. A. Smith, J.M. Laurent, D.S. Smith, R. Rodriguez-Clemente, Thin Solid Films, **266** (1995) 20-30.

EVOLUTION OF THE MICROSTRUCTURE AFTER HEAT TREATMENT OF OPTIMALLY QUENCHED Nd-Fe-B

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The advantage of using the rapid quenching technology for obtaining high - coercive Nd-Fe-B magnets is reflected in the possibility of directly influencing the grain size and microstructure through the quenching speed with the aim of achieving a magnetic microstructure, which provides maximal magnetic energy of finished magnetic materials of this type. The cooling rate range in which optimal results are achieved is rather narrow so that heat treatment of melt-spun Nd-Fe-B alloys is needed in order to achieve the maximal coercivity. The study is extended to investigate the effects of the most convenient regime of heat treatment for the optimal selected cooling rates for tested Nd-Fe-B alloys. The evolution of the microstructure after heat treatment in melt–spun Nd-Fe-B alloys with a different Nd content is observed. The phase analysis was determined by powder X-ray diffraction and Mossbauer spectroscopy phase analysis. For determining the critical temperature of phase and magnetic transformations thermomagnetic measuremnts (TM) were carried out on a vibratory magnetometer. The thermomagnetic curves contained completed hysteresis loops in stages before and after TM treatment. Two different kinds of the melt-spun material with different compositions (one almost monophase while the other with a pronounced composite structure) and slightly different heat treatments have been studied from the point of view of their quality as hard magnetic materials and of their corresponding structure. The results of X-ray analysis, Mossbauer spectroscopy together with thermomagnetic measurments for investigated Nd-Fe-B alloy compositions heat treated in an optimal regime are presented in order to bring some new information concerning the relation between their structure and magnetic properties.

MICROSTRUCTURE MODELING OF A CERAMIC TILE SYSTEM

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Structural inhomogenities in the case of ceramic tiles are not "visible" in the stage of green state [1], but later they create serious defects during drying and firing processes [2-3]. This paper contains an analysis of their influence on the microstructure of final products with the aim of understanding the formation of base crystal forms as well as the distribution of the amorphous phase during the firing process. Easily detectable macro characteristics of the final products, such as water absorption, diametrical strength and frost resistance are used in the procedure of screening the complete ceramic system. The results obtained on the micro level, freezing dilatation and scanning calometry values, emphasized the critical temperature interval for frost resistance of the defined product microstructure guiding the changes of processing parameters.

1. J. Ranogajec, R. Marinković, K. Kasaš, B. Živanović, Correlation between atomized powder composition and final tile composition, Am. Ceram. Soc. Bull., **21** (2) (1992) 208.
2. M. Radeka, J. Ranogajec, R. Marinković-Nedučin, Compaction Mechanism as the Function of Atomized Powder Particle Size, Ceram., Inter., **21** (1995) 249.
3. B. Barat Hip, A. Karh Domonkoš, R. Kilibarta Šobotić, L. Aroksalaši, J. Ranogajec, Design of Green and Fired Microstructure of Ceramic Wall Tiles, Key Engineering Materials, **206-213** (2001) 1783.

STRUCTURAL AND PERCOLATIVE PROPERTIES OF ELECTROCONDUCTIVE Si_3N_4 - TiN CERAMICS

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Sintered Si_3N_4-TiN ceramics are among the most interesting engineering ceramics for high temperature application, because of their high strength, hardness and thermal stability. The addition of TiN improves the fracture toughness of Si_3N_4, and for appropriate amounts of TiN, Si_3N_4-TiN composites show high electrical conductivity making them suitable for electrical discharge processing. The concentration of TiN at which the electrical resistivity drastically drops from 10^{-10} Ωm for Si_3N_4 — 10 % TiN to 10^{-2} Ωm for Si_3N_4 — 35 % TiN is called percolation concentration. The percolative behavior of electroconductive composites is investigated as a function of microstructural characteristics and the applicability of various proposed models has been discussed. The microstructure of composites, sintered with different sintering aids and amounts of TiN, have been investigated using SEM and EDS systems. Computer simulation of conductivity-concentration curves has been done for a conductive network, which can be presented as a two or three-dimensional lattice. The relation between the critical power exponent of conductivity and starting powder diameters for different types of lattices along with the effects of volume percolation concentration were also investigated. Better agreement between theoretical and experimental results has been obtained using a two-dimensional network for which the critical power exponent has been proposed.

EVOLUTION OF THE MnZn-FERRITE MICROSTRUCTURE BY APPLYING OF A THIN LIQUID-PHASE FILM

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Liquid-phase assisted microstructure evolution (LPAME) is often mistakenly believed to be fully developed in all fields of science, technology and applications. However, the truth is that although (LPAME) has a long history and has been the subject of intensive investigations in the past, because of their technical importance, it remains the focus of intensive research. This is particularly so for application of (LPAME) during microstructure evolution in MnZn-ferrites, where the initial permeability (μ) can be significantly improved through (LPAME). We have investigated the effect of liquid phase film formation on the microstructure development during sintering of MnZn-ferrite (MZF) and their magnetic permeability. Our results revealed that the microstructure and the final magnetic permeability depend on the thickness of the liquid-phase film formed during sintering. The solution - reprecipitation (S-R) process, which is associated with an intensive microstructure development in MZF starts when a continuous liquid-phase film of critical thickness δ_o, which wets the MZF grains is formed. The solid-state sintering that takes place prior to the formation of the critical liquid-phase film is essential for the final microstructure in liquid-phase-assisted sintering of MZF.

SINTERING OF SMALL PARTICLE CERAMICS: RELATION BETWEEN GRAIN GROWTH AND RELATIVE DENSITY

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In several oxide-based systems, it has been shown that grain growth and densification can be related phenomena. When considering the sintering of small grain powders, it generally starts by a matter transfer at the grain interface. In the absence of a liquid phase formation, the dominant mechanisms are surface diffusion and/or grain boundary diffusion, which are both very sensitive to surface segregation such as the presence of an additive. A detailed study of SnO_2 doped with MnO_2 has shown that the first matter transfer during heating, which corresponds to surface diffusion, favors grain growth and then an increase in surface additive concentration. When a critical concentration is reached, grain boundary diffusion becomes preponderant and shrinkage occurs. During the complete densification process, we have noticed a linear relationship between $1/\rho$ and $1/D$ where ρ and D correspond to the relative density and the average grain size, respectively. This relationship is valid for other systems such as SnO_2 doped with Fe_2O_3, Al_2O_3 doped with MgO, Y_2O_3 doped with TiO_2 or UO_2 doped with TiO_2. The interest is to be able to predict the final microstructure of ceramics prepared from nanometric powders until abnormal grain growth occurs.

1. D. Gouvea, J.A. Varela, A. Smith, J.P. Bonnet, Densification and coarsening of SnO_2 based materials containing manganese oxide, J. Eur. Ceram. Soc., **18** (4) (1998) 345-351.
2. L. Pennisi, Master Thesis, Alfred University, USA, 1978.
3. C. Gregovich, K.W. Lay, Grain growth in very porous Al_2O_3 compacts, J. Am. Ceram. Soc., **80** (5) (1981) 147.
4. G. Gasgnier, PhD thesis, University of Limoges, France, 1991.
5. S. Bremier, PhD thesis, University of Limoges, France, 1997.

SYNTHESIS AND CHARACTERIZATION OF AMORPHOUS COBALT POWDERS

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Amorphous metal powders are well known to have a much larger active surface than the crystalline forms of the same metals. This is widely used to create special materials to be used for catalysis, hydrogen storage, surface reactions and many others. We have synthesized amorphous cobalt powder by reduction of cobalt-chloride, using hydrazine, at a high temperature and pH value. The thus obtained powder was enhanced, placing nanoparticles of Pd and Pt on the surface of metallic grains. Our optical microscope examination of these powders shows that the grain size varies from under 1 to 20 μm, with their area varying from 1 - 200 μm^2. We have also found that the powders are very good at hydrogen absorption. We have also conducted photoacoustic, SEM and X-ray diffraction analysis and sintering under various conditions. We have, then, conducted a thorough analysis of the sintered samples to find out exactly how their properties changed after the sintering.

LASER SINTERING OF AS-COMPACTED SiO_2 POWDER: EVOLUTION OF THE POROUS STRUCTURE COMPLICATED BY LOCAL DENSIFICATION

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The evolution of the porous structure in as-compacted SiO_2 spherical powders during laser sintering was studied. Particles of 0.3 - 0.4 μm in diameter were sintered under CO_2 laser beam (λ = 10.6 μm, power density of 100 Wt/cm^2). Liquid phase sintering took place due to surface melting of particles and followed

rearrangement of solid cores in the melt. In the green compact, the particles were inhomogeneously distributed through the specimen and therefore, density was inhomogeneously distributed as well. Particles grouped into aggregates of 2 - 3 μm, formed coarse agglomerates of 5 - 10 μm in size. In the structure of green specimens one can distinct the following types of pores: (1) coarse pores of ~3 μm between agglomerates, (2) pores of average size ~1 μm between aggregates, (3) small pores of ~ 0.05 μm between loosely packed particles and (4) submicropores (~ 0.02 μm) between closely packed particles. Such a highly complicated microstructure of the green specimen evolves inhomogeneously in the course of sintering: coarsening of grains due to intensive coalescence and gradual decrease of size and number of pores. The intensive differential densification on the initial sintering stages is a result of a large difference between intraagglomerate and ineragglomerate shrinkage rates. Local melting and rapid rearrangement of grains under laser heating conditions (large gradients of temperature and stresses) cause a high densification rate within primary agglomerates. This rate differs from the integral one of the specimen as a whole and this difference becomes a reason for local densification.

A COMPARATIVE STUDY OF INTERFACE PROCESSES AND INITIAL GROWTH STAGES OF Bi – BASED FILMS PRODUCED BY THERMAL EVAPORATION AND SELF-ION ASSISTED DEPOSITION

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Bismuth is a promising material for metallic nanoelectronics. One of the limitations is caused by the quite short conduction electron mean free path (less than 100 nm) in submicron Bi films, thus ensuring fast device operation. In [1-3] submicron Bi films 50 – 60 nm thick with a conduction electron mean free path of 1.5 microns were obtained for the first time. These film properties were explained by the strong influence of the structure of grain boundaries arising during evaporation and/or recrystallization on the electrical resistivity of the submicron Bi

films. The present work deals with an investigation of initial stages of the growth of (Bi, Bi–Sb) films produced by methods of different degree of nonequilibrium, such as thermal evaporation (TE) and self-ion assisted deposition (SIAD) [4-5]. The comparative analysis of interface thermodynamics, growth mechanisms and film island evolution (faceting and coalescence) was carried out depending on the type (crystalline, amorphous) and temperature of substrate, evaporation rate, film composition, etc. Ion assisted deposition leads to films of a higher density and reduced porosity, greater stability than those deposited without ions. As compared with pure Bi films the facetted island morphology of the self–ion deposited Bi–Sb (20 %) films is not so clear. This is explained by a partial realization of the coalescence process by a liquid fluidity mechanism. At all substrate temperatures the film grain orientation (111) R is more pronounced for self–ion assisted deposition than for thermal evaporation.

1. A.I. Il'in, A.V. Andreeva, B.N. Tolkunov, J. Advanced Mater. **3** (1996) 33.
2. A.I. Il'in, A.V. Andreeva, B.N. Tolkunov, Mat. Sci. Forum **207-209** (1996) 625.
3. A.I. Il'in, A.V. Andreeva, Metal Phys. & Mat. Sci., **60** (1995) 131. (in Russian, translated in English)
4. O.V Kononenko, V.N. Matveev, A.Yu. Kasumov, N.A. Kislov, I.I. Khodos, Vacuum, **46** (1995) 685.
5. O.V Kononenko, A.V. Andreeva, A.I. Il'in, V.N. Matveev, Texture & Microstructure of Magnetic and Electronic Films, Materials of the MRS Meeting, USA, San Francisco, 2002.

A CONTRIBUTION TO THE PROGNOSIS OF SOME MICROSTRUCTURE FEATURES OF SINTERED CERAMIC MATERIALS

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As it's known, just the union of experimental and theoretical data enables prognosis of properties of sintered materials. In that sense, a model based on the infinite atom chain has been considered. It is very convenient for consideration of crystalline and electronic structure of sintered ceramics. Using the data on energetic parameters for the directions and planes and other entities of the crystalline structure, the numerical values of some characteristics of sintered-$BaTiO_3$ were determined. On the basis of them, we can predict structural changes during the sintering process.

A REVIEW TO THE DATABASE OF CERAMIC SINTERED MATERIALS MICROSTRUCTURE

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One of the features of the formed database is that the elements and alloys share characteristic groups. In this group, a specific role is taken by particular data levels of the structural hierarchy. Taking prognosis of the properties of ceramic sintered materials into account when considering microstructures, which represent one of basic sections, in this paper, our results on the connection with that section were presented.

A NOVEL METHOD FOR DETERMINATION OF THE DIHEDRAL ANGLE IN SnO_2 CERAMICS

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Analysis of the sintering mechanism should take into account some geometric parameters, for example, neck grain growth, grain size, porosity and the dihedral angle. The dihedral angle reflects energy limits, as well as mobility of the grain boundaries. It is more convenient to determine the dihedral angle in materials that show anisotropic growth during the sintering process. The aim of this work was to determine the dihedral angle for SnO_2 ceramics doped with MnO_2. Generally, a kinetic study of this ceramics is limited, due to a high anisotropy during sintering. Investigation of grain growth as well as measuring of the dihedral angles was performed by statistical analysis of the results of atomic force microscopy. The calculated value of the dihedral angle was 129.22° (± 1.38°).

STRUCTURAL AND MORPHOLOGICAL PROPERTIES OF THE AMORPHOUS SiO_2 PRECIPITATE AFTER THERMAL TREATMENT, AS A CONSEQUENCE OF THE PRECIPITATION TEMPERATURE

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The amorphous SiO2 precipitate, obtained in the process of neutralization of hydrated sodium silicate by the means of sulfuric acid, exists in an agglomerated state. Agglomerates, with an approximate average diameter of 20 μm, consist of primary particles of nanometer size. Depending on the precipitation temperature, which ranged from 80 – 95°C, 20 - 50 nm particles, in the sample obtained at 80°C and 50 - 100 nm in the sample obtained at 95°C, have been generated. The size and energy state of primary particles, as well as of agglomerates, provoke different behavior of the precipitate, when exposed to thermal treatment at 1100°C with varying duration. The differences consist of the following: size of primary particles, specific surface, stability of agglomerates, morphological changes of particles, ability of structure ordering (i.e. crystallization). The properties mentioned above have been analyzed by the means of the following instrumental methods: scan electronic microscopy, laser granulometry, XRD, and specific surface area (by N_2 and H_2O). The foregoing results corroborated different properties as well as structural transformations of the obtained amorphous precipitate samples at 80 and 95°C.

THE EFFECTS OF SUBSTRATE TEMPERATURE ON THE STRUCTURAL PROPERTIES OF SnO_2 THIN FILMS DEPOSITED BY THE PYROSOL PROCES

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Tin oxide thin films were deposited on glass substrates from a $SnCl_2 \cdot 2H_2O$ alcohol solution by the pyrosol proces. The films were prepared for different substrate temperatures (300, 350, 400 and 450°C) and the obtained film thickness was in the range of 390 – 560 nm. The structure and morphology of deposited films were investigated by X-ray diffractometry and scanning electron microscopy. Parameteres of the crystal lattice and preffered orientation of films were calculated and the dependence of the substrate temperature was established.

INFLUENCE OF THE DENSITY OF IRON COMPACTS ON THE THICKNESS OF BORIDE LAYERS

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The results of the paper are a contribution in the study of the boroning process of P/M materials based on iron. This paper presents a mathematical model describing the influence of pressing pressure and particle size of the iron powder on the boride layers depth with the application of regression analysis. The examination has been performed on pressed samples of iron powder of a chosen particle size distribution. The specimens were pressed under pressures of 200, 400, 600, 800 and 1000 MPa. Boroning was performed in a solid mixture on the boron-carbide basis, and was in principle the same for all samples. An optical microscope was used for microstructural characterization of boroning samples and to measure layers depths. The obtained boride layers vary in depth and quality (porosity, the contact with metal). Investigation results show that after increasing pressing

pressure and powder particle size the boron layer depth decreased. Specimens with a high layer depth were obtained with the pressure of 200 MPa. The powder particle size and pressed pressure have an influence on the boride layer quality. Increase of these parameters leads to an increase of compact boride layers and decrease of total porosity. Satisfying density values were attained on pressed samples under pressure of 1000 MPa. It has been observed that simultaneously with boroning sintering also occurred, and this fact offers a wide application possibility in the chemical-thermal treatment for P/M materials. The decrease of porosity of boron specimens is a result of activated sintering.

CHARACTERIZATION OF ZINC STANNATE CERAMICS MICROSTRUCTURE USING A NEW DIGITAL METHOD

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Spinel zinc stannate (Zn_2SnO_4) is a promising material with various applications, such as sensors, window coatings or transparent electrodes. Porous semiconductor ceramic sensors based on n-type oxides are often used for detection of gases and moisture, where the sensing mechanism is a surface reaction between the material and the environment. Within this feature the microstructure is a considered a very important parameter. Proper control of a materials microstructure, i.e. grain and pore size distributions, porosity and surface area is essential for a high sensitivity. In this work, a new digital method is used to correlate synthesis parameters with the obtained sintered zinc stannate microstructure and establish the correlation in the triad "synthesis-structure-properties".

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