

RIGA TECHNICAL UNIVERSITY

ILONA PAVLOVSKA

**PREPARATION OF HYDROXYAPATITE
NANOPOWDERS AND COMPOSITE
CERAMIC USING SOL-GEL METHOD**

Summary of Doctoral thesis

RIGA 2006

Topicality of the theme. Today the demand for implants which guarantee filling out the bone defects and allow a definite reaction of the cells, that is, allow the bone tissue to grow into the implant is increasing. Bioactive ceramics such as hydroxylapatite (HA), α - β tricalcium phosphates (α -TCP, β -TCP), tetracalcium phosphates and bioglass are recognized as such materials. Ceramics interacts with body tissues and takes part in the biochemical processes as well, therefore it should not only be dense and strong, but also with a definite structure of pores which guarantee growing of the bone into the implant. HA has been recognized as the best material because it is biocompatible with bones and it does not dissolve fast in the body as well as does not decompose fast. However, it has bad mechanical qualities, and therefore it is not used as a monolite implant but as a coating on metal (aluminium, titanium and alloys of titanium) or silicate substrates. The coating of HA should have a mutually connected structure of pores with the diameter of 100 μ m for bone tissues to grow and strengthen themselves at the implant. As a result, a coating should be at least 100 μ m thick.

HA is obtained with different methods which determine the degree of crystallinity and the size of the grains. Compared to the traditional methods of powder caking, the process of sol-gel is the most perspective method for obtaining ceramic materials. HA can be obtained at a lower temperature of synthesis using the process of sol-gel. In addition to this, the obtained hydroxylapatite has a higher degree of homogeneity and a lower quantity of other substances.

It is very difficult to obtain material with a large quantity of mutually connected open pores and sufficient mechanical strength at the same time, therefore the main task was to develop bioceramics with different sizes of pores and their distribution. This kind of ceramics has several advantages, for example, the pores of different sizes generate even transfer of the load and diminish the problem of the voltage shield to the minimum. It is possible to increase chemical homogeneity and microstructural evenness for the composites based on HA using nanotechnologies.

Great part of the paper has been based on tasks carried out within the boundaries of project "Multifunctional percolated nanostructured ceramics fabricated from hydroxylapatite" of the 6th frame program of European Union.

Samples were sent to 13 project partners:

- EROTHITAN Titanium implants AG, Germany (PERCERAMICS application for bioimplants);

- Hungary, University of Budapest of Economic Sciences and State Management (immobilisation of yeasts);
- University of Telaviv, Israel (electrical charging, immobilization of bacteria);
- Institute of Microbiology and Biotechnology of University of Latvia, Latvia (immobilisation of yeasts);
- Waste Management Association of Latvia, Latvia (PERCERAMICS application in solving problems of cleaning the environment);
- Lodza Technical University, Poland (immobilisation of yeasts and bacteria of milk acid);
- The Centre of Orthopaedics and Medicine, Medicine Academy of Tomsk, Russia (production of PERCERAMICS, preclinical checking of bioimplants);
- The Institute of Researching Mathematical Problems of Biology of Science Academy of Russia, Russia (modelling of HA nanoparticle computer, research of the character of charging and adhesion/cohesion);
- Zhytomir State Technical University, Ukraine (comparing of PERCERAMICS results);
- Abertau Dundee University, UK (research of biological properties);
- VIRECO Ltd, Hungary (application of immobilised yeasts for biofilters for sorption processes of heavy metals).

The aim of the paper. The paper is tended to solve the two main problems which determine the ability of the cells to stick to the surface of the material and possibilities of ceramics usage, those problems are called porosity and endurance. The first problem is appropriate porosity which should provide parts of ceramics surface with the sizes of pores which are suitable for cell receptors. Pores form the net of the canals which facilitates the change of metabolites around a fixed cell. Endurance is connected both with the chemical endurance in the solutions of different pH and the mechanical endurance.

Tasks. The paper consists of four main consistent parts which include solving the following problems:

- reparation of HA nanopowder, using the solution method and grinding obtained powder in a planetary ball mill;
- preparation of HA ceramics using nanosize HA powders;
- synthesis of the sol-gel compositions using the systems $\text{TiO}_2\text{-SiO}_2$ and $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$;
- preparation of HA/sol composite ceramic.

Different sizes of the particles of hydroxylapatite powders, the influence of thermal treating of dry-pressed powders on the annealed ceramics of hydroxylapatite and the resulting structure of ceramics, possibilities of using compositions of partly hydrolyzed sols of alcoxides and their influence on the structure and properties of the end product have been researched in the experimental part.

The morphology of the ceramic surface has been evaluated by studying the samples by the methods of optical, atomic force and scanning electron microscopy. Research of material structure has been done using the methods of X-ray diffraction and infrared absorption spectroscopy. In order to characterise the mechanical properties of the obtained materials such characteristics as the compression strength, the modulus of elasticity, the volume weight and the apparent porosity have been determined. The chemical durability has been studied by the behaviour of the ceramics in the solutions of different pH for various times.

Dependence of the properties on the way of modification of the used composition and technological parameters of its obtaining has been studied.

Scientific significance and main results. Grinding the hydroxylapatite powder obtained by the solution method gives a possibility to obtain nanosized hydroxylapatite powders whose particle size varies from 10.00 μm (6 h) to 0,03 μm (24 h). The larger particles can be separated by sieving and the size of dominant particles that vary from 3 nm to 63 nm could be reached.

It is possible to obtain the increased strength characteristics for the pressed HA ceramics pressing ceramics from the mixtures of different size powders.

For the preparation of composite ceramics compositions of sols were synthesized in the systems of $\text{TiO}_2\text{-SiO}_2$ and $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$.

Using the partly hydrolyzed solutions of alcoxides for preparing the composite ceramics in the systems $\text{TiO}_2\text{-SiO}_2$ and $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$ the ceramics with excellent parameters of apparent porosity and compression strength has been obtained: $V_a = 34 \%$, $\sigma - 730 \text{ MPa}$.

Research connected with the application of surface active substances confirmed the usefulness of their usage as they helped form the structure with more even distribution of pores increasing the apparent porosity by 13 % and not influencing the strength parameters.

It is stated that the mode of drying and annealing has considerably influenced the structure and properties of the composite ceramics. A slow burning mode (2 $^\circ\text{C}/\text{min}$, with a slow increase of the temperature at the beginning of burning to 400 - 600 $^\circ\text{C}$) guarantees the

possibility to obtain HA ceramics with nanosize particles of hydroxylapatite. It is obvious during a case of slow burning that the process is connected to a successful process of a secondary recrystallization of HA guaranteeing the compatibility of ceramics structure to the crystalline phase of hydroxylapatite.

In a case of the composite ceramics it is possible to achieve 38 times higher parameters of chemical endurance in different media of pH in the stationary and the dynamic mode of determining chemical durability compared to the pressed HA powder ceramics.

The results of the partners of the project PERCERAMICS "Multifunctional percolated nanostructured ceramics fabricated from hydroxylapatite" confirm wide usage possibilities of the obtained product in medicine, food processing, improving the ecological situation of the environment, technologies of water cleaning etc.

Theoretical background. The data about the properties of bioceramics, preparation methods of hydroxylapatite, peculiarities of the drying and heating process, possible methods of applying bioceramics coatings, preparation of ceramic using sol-gel method - hydrolysis, condensation and polymerization, drying and sintering processes were summarised in literature review.

The sol-gel systems of ZrO_2 , TiO_2 and SiO_2 have been described both in separate and combined systems as well as their properties and possibilities of their forming. Attention is paid to the transition sol-gel and the explanation of the process of gel forming. Interaction of hydroxylapatite with tissues of a human body, decomposition and sequence of crystallization has been described. A wide range of applications of sol-gel and bioceramic materials have been mentioned.

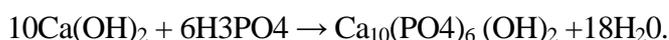
According to the data one can conclude that the sol-gel technology is a progressive method. It gives better properties for fabricating porous ceramics and coatings than other methods thanks to the relatively simple process, low fabrication costs and possibilities of controlling the whole process allowing to synthesis suitable materials for a particular application. The sol-gel technology at its present state of development gives the most chances to manage the structure transformations which take place during the synthesis of glasslike, ceramics and coating materials.

The aim of biomedicine is to work out and develop artificial materials or "spare parts" for a human body in order to evaluate, to renew and to improve physiological functions or to prolong survival functions and their quality.

The data confirm prospective application of hydroxylapatite ceramics in orthopaedic surgery. It is necessary to continue the research of different kinds of hydroxylapatite ceramics for practical application in accordance with its physical and chemical parameters.

The world turnover of biomaterials is about 50 billion euro every year (an increase of turnover may be 8 - 40 % a year).

Methodology. Two kinds of HA powders were used for the research (the first was synthesized mechanically chemically, but the second was synthesized by the solution method). The HA powder was fabricated by the solution (H.Aoki) method, that means, in the reaction of calcium hydroxide [Ca(OH)₂] water suspension with the phosphoric acid [H₃PO₄]:



For fabricating of HA ceramics the dry powder pressing was used (applying the forms of two-size diameters - 5 mm (little platelets) and the diameter - 10 mm (big platelets). Pressing was performed by two-stage powder packing applying a table press with a manual hydraulic lead (SPRUT 10/185, Latvia). After pressing the ceramic were heated at 1100 °C temperature with temperature increasing rate of 5 °C/min, and annealing at this maximum temperature during 1 hour.

In order to prepare sols within the systems of TiO₂-SiO₂ and ZrO₂-TiO₂-SiO₂ the following reagents with mark "chemically clean", "clean for analysis" were used: tetraethylorthosilicate 98 % (C₈H₂₀O₄Si-TEOS, ACROS), izopropoxide of titanium (IV) 98 % (C₁₂H₂₈O₄Ti - TiPrⁱ, ACROS), ethoxide of titanium (IV) 33 - 35 % (C₈H₂₀O₄Ti - TiEt, ACROS), izopropoxide of zirconium (IV) 98 % (C₁₂H₂₈O₄Zr - ZrPrⁱ, ACROS), izopropanol (C₃H₇OH - nPrOH, ACROS), buthanol (C₄H₉OH - BtOH), ethanol (C₂H₅OH - EtOH), acetic acid (ice) - (CH₃COOH - HOAc, ACROS), oxalic acid (C₂H₂O₄·2H₂O - Reahim), glycerol (C₃H₈O₃ - Reahim), ethylene glycol (C₂H₆O₂ - Fluka) and fine disperse additives: SiO₂ (Ø - 0.007 µm, ACROS), ZrO₂ (Ø - 0.325 µm, ACROS) and TiO₂ (Ø - 0.325 µm, ACROS).

To prepare the solutions (sols) the reagents in different molar ratios were used. The sols studied in the present work were prepared in the wide range of initial component composition - xZrO₂-yTiO₂-(100-x-y) SiO₂ (x= 10-60 (mol %), y =15-40 (mol %) and xTiO₂-(100-x) SiO₂ (X= 10-90 mol %) in the systems of sol-gel using ethanol, izopropanol and buthanol as mutual solvents, and adding water or without it as also using modifying additives such as oxalic acid and fine dispersed powders of ZrO₂, TiO₂ and SiO₂.

For the measurements of sol viscosity a rotation viscosimeter VT550 (Thermo Haake Electron corporation, Germany) with a sensor MV-DIN was used. The used shear rates were ~ 100 -800 rev/min (multiplications of the rate with one of the geometric parameters of the sensor). The time of gelation (T_{gel}) was determined as the time when toppling the beaker with a forming gel at angle of the 90° , the sol (gel) does not change the state of its surface in accordance with the walls of the beaker.

Preparing sol-gel matrixes for fabricating HA composite ceramics some researched sol compositions in the systems of TiO_2 - SiO_2 and ZrO_2 - TiO_2 - SiO_2 were chosen. In order to obtain sol - gel ceramics with a distinct network of channels and larger pore sizes compared to the pressed HA ceramics different volume ratios of HA/sols were used: 1:10, 1:4, 1:3,2:3, 1:2,4:1, 1:1,2:1,3:2,3:1,4:1, 10:1. The prepared composite compositions were poured into cylindrical forms of polymer material (diameter - 30 mm, height - 50 mm) and dried at the temperature of $60^\circ C$ for 72 h and then annealed at various temperatures up to $1100^\circ C$.

The analysis of X-ray phases (RTg) was performed with diffractometers DRON-3 and DRON-6 (Russian Federation) using the radiation of a copper cathode (Cu) Ka. Samples before the analysis of RTg were held at different temperatures, finely grounded in an agate mortar and glued to a glass plate by PVA glue. The identification of the phases was performed according to the data of ASTM X-ray metric card index.

Infrared absorption spectroscopy (IS) measurements were done by the equipment Specord 75 IR (Carl Zeiss, Germany). Spectra were recorded in the range of 1600 cm^{-1} to 400 cm^{-1} . Samples were prepared in the form of pills pressing the studied substance together with a powder of KBr.

Differentially thermal analysis (DTA) was performed on a MOM (Pauling - Pauling, Hungary) derivatograph. The sample weight for DTA research was from 0.3 to 0.6 g, the heating rate was 5 / min.

In order to determine the linear change of sizes of the annealed sample the thermal treatment shrinkage of the samples was measured. The linear sample sizes were determined using a micrometer (Mitutoyo Digimatic micrometer, Japan). The thermal treatment shrinkage was calculated in per cent from the diameter and the height of the dried example.

The method based on the principle of Archimedes described in the standard LVS EN- 623-2 was used to determine the apparent porosity of the ceramics.

Visual examination and assessment of synthesized powders and ceramic platelets was performed by stereomicroscope Leica M 420 (Leica Wild Macroscope, Switzerland) and digital camera Leica DC Camera (magnifications used x20 and x40, software Image-Pro Plus 5)

The chemical durability of the HA samples was determined immersing the ceramic samples in the certain pH water solutions (static method) and stirring the ceramic samples in the solutions (dynamic method) with a various value of pH (pH - 2, 4, 6, 8). HCl was used for preparing acidic solutions and NaOH - preparing basic solutions. A magnetic stirrer (VELP Scientifica, Italy) was used for stirring. The samples were immersed in the solution for 1 hour with a stirring rate 5. Some samples were immersed in the solutions at the room temperature, but some experiments were performed combining stirring with heating to 60 °C.

Scanning probe microscope VEECO SPM II (USA) was used for the atomic force microscopy (AFM) studies of samples. The contact and tapping modes were used for measurements. VEECO Nano -tips made from Si₃N₄ were used. The spring constants were 40 N/m and 0.9 N/m. The following parameters were used for the tapping mode: the length of the cantilever - 125 μm the resonant frequency during measurements was 300 kHz, for the contact mode the length of the cantilever was 250 μm, the resonance frequency during the measurements was 25 kHz. For the measurements both in the tapping and in the contact mode the radius of the tip was 10 nm and the voltage applied - 1.1 V. The areas of the samples measured were 30x30, 25x25, 10x10, 5x5 and 1x1 μm².

The morphological research of xerogel and composite ceramic samples as also evaluation of synthesized powders was performed with a scanning electron microscope (SEM) T200 - JEOL (Japan). The samples were coated with a carbon or with an Au/Pd layer in high vacuum.

The compressive strength and the module of elasticity of the materials were measured by the universal testing equipment UTS 100 (Russian Federation) in accordance with EN ISO 527 at the deformation rate of 5 mm/min.

The hydrophobicity of the surface was studied measuring the contact angle of a drop of distilled water immediately after its contact with the sample surface (the wetting angle was measured at the Department of electrotechnique and electronics of the Faculty of Engineering, Telaviv University (in the framework of the project ESF STRP504937 - 1 "PERCERAMICS"). Determination of the wetting angle was performed with a microscope Olympus MX-50 (USA) which was equipped with an in-built camera and a program of taking digital photos. The procedure of

determining wetting angle was performed in the box with a constant temperature - 26 °C and the relative humidity of $45 \pm 5\%$.

Experimental part I: Preparation of hydroxylapatite nanopowders. Two types of differently prepared HA powders (the first one prepared by the solution method, while the second one - by mechanical chemical method) and ceramics obtained from that are compared in the present paper. The HA powder $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ prepared by the solution method after 72 hours drying was ground in a corundum planetary ball mill during 1, 6, 12, 18, 24 and 36 hours. Denominations of HA powders used are summarized up in the Table 1.

The second kind of HA powder was synthesized in the Centre of Orthopaedics and Medicine of the Medicine Academy of Russian Federation using the mechanically chemical method.

It is supposed that grinding of the powders of hydroxylapatite and tricalcium phosphates using a ball mill increases the ability of the powders to react and decreases the temperature of the synthesis [1].

The powders were ground for 1, 6, 12, 18, 24 and 36 hours in order to fabricate powders of a different degree of dispersion and to determine the influence of the degree of dispersion of HA powders on the forming processes of the texture of composite ceramics.

Table 1
Preparation of HA powders synthesized by the solution method

Sample	Duration of grinding, h
HA	HA powder dried for 72 h, ground in an agate mortar
6h	HA powder ground in a planetary mill for 6 hours
12h	HA powder ground in a planetary mill for 12 hours
18h	HA powder ground in a planetary mill for 18 hours
24h	HA powder ground in a planetary mill for 24 hours
24hS	HA powder ground in a planetary mill for 24 hours and sift through the 0.063 sieve
36h	HA powder ground in a planetary mill for 36 hours
6+24h	the mixture of the 6h powder and 24h powder (50/50)

The data of optical microscopy confirm efficient break down of HA agglomerates (Figure 1).

The measurements of the particle size showed that prolonged grinding increases polydispersion of the particles. After 6-hour grinding 87 % of the observed particles had a size of 5 - 7.5 μm and the others had a size of more than 7.6 μm , but after 36 hour grinding 17 % of resulting particles had a size of 3.6 to 5.0 μm , 27 % had size of 5.1 to 6.5 μm , 45 % had a size of 6.6 to 7.9 μm and 11 % with the size of more than 7.9 μm . Braking

down of the initial HAp agglomerates takes place within 6-18 hours of grinding.

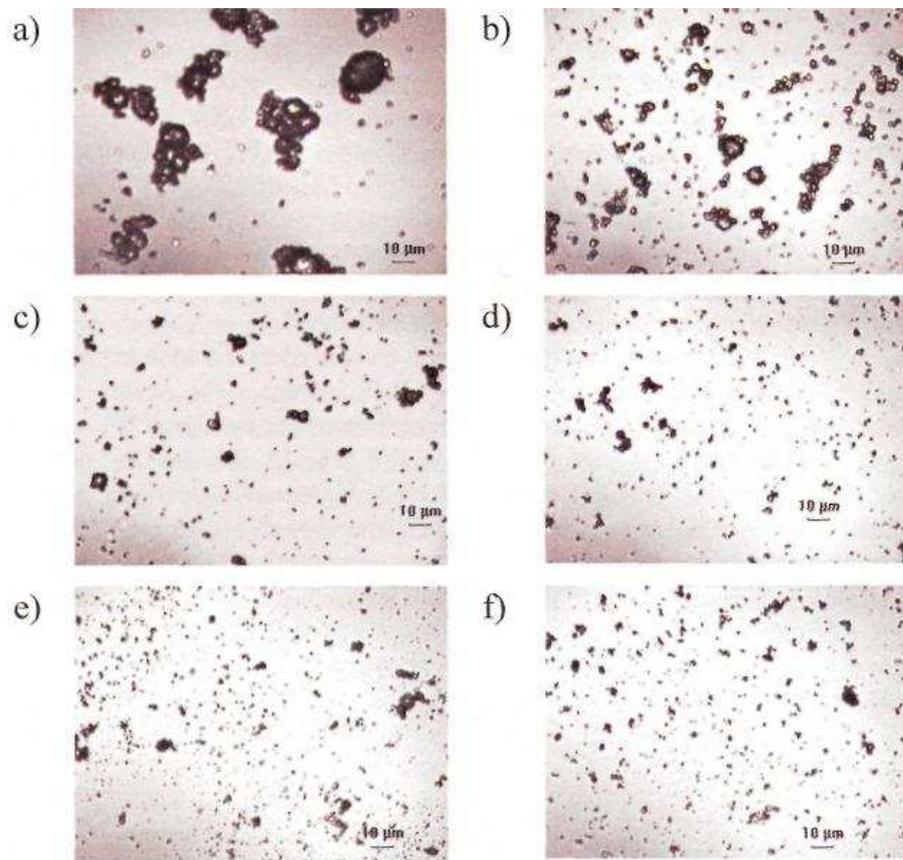


Figure 1 The images of optical microscopy of HA powders prepared by the solution method. Duration of grinding in a planetary ball mill: a) - 1 h; b) - 6h; c) - 12h; d) - 18 h; e) - 24 h; f) - 36h.

Table 2

Particle size of HA powder determined by SEM

Sample No.	Sizes of powder particles determined by SEM method, nm
6h	300 nm – 10.00 µm
12h	50 nm – 200 nm
18h	50 nm – 150 nm
24h	30 nm – 100 nm
24hS	3 nm – 63 nm
36h	30 nm – 900 nm

The results of optical and electronical microscopy confirm the observation described in the literature about reagglomeration caused by long grinding [22].

Experimental part II: Preparation of HA ceramic using nanosized HA powders. In order to get an insight of suitability of mechanically activated HA powders differing in fineness for the development of ceramic materials, they were dried at 100 °C for 72 hours after grinding in the planetary ball mill. Dried and ground at different time intervals HAp powders were pressed into platelets with a diameter 5 mm and thickness 2-3 mm at 250 and 375 MPa. Platelets were annealed at 800, 1000, 1100 and 1200 °C for 1 hour.

The results of SEM confirm the suitability of HA powder grinding to form the pore structure of the ceramic materials (Figures 2, 3). The size of powder particles determines the development both the nanosize (micropore) and the micrometer (macropore) size of pores in the process of ceramic sintering.

The research results of optical microscopy and SEM analysis gave a possibility to compare the morphological peculiarities of the pressed ceramics surface of differently synthesized HA powders (24HS, 6h, T36, 29A, 33M, and 31 SM) which are connected with the presence of micro and macro pores.

The results of microbiological research performed by the partners of PERCERAMICS project (National Centre of Scientific Research (France), Budapest University and VIRECO Ltd. (Hungary), Telaviv University (Israel), Institute of Microbiology and Biotechnologies, Waste Management Association of Latvia (Latvia), Lodza Technical University (Poland), University of Abertau Dundee, UK) showed the suitability of ceramic materials 24hS and 29A for the determined purposes of HA immobilized cell and bacteria application in various technologies, which could be related to the presence of macroscopic pores.

This fact confirms also that by grinding of hydroxylapatite synthesized by the solution method it is possible to obtain the powder with similar particle sizes and the chemical activity as in the case of preparing HA powders by the mechanical chemical method. In order to determine the porosity of the synthesized ceramic the method of analysis of AFM data was also used. The data obtained by the AFM analysis (Table 3) correspond well with the porosity data obtained by the standard method. The exception is 24 hS ceramic whose AFM porosity is two times more. It points to the presence of mainly nanosized pores in the material which could not be detected by the standard method of porosity determination.

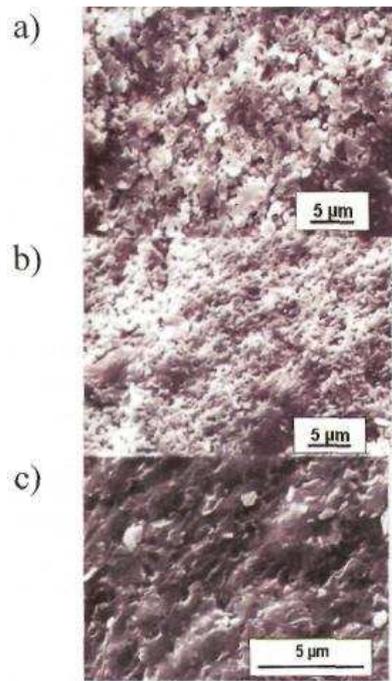


Figure 2. The results of the SEM analysis of the annealed HA ceramics 1100°C (cross section) which is obtained by the grinding during: a) - 6 h; b) - 36h); c) - 24 hS



Figure 3. SEM micrograph of 24 hS powder which is used for fabricating ceramics

Table 3

The comparison of the porosity results

Method	The standard method of ceramics porosity measurement (LVS EN 623 - 2), %	Determination of porosity by AFM results analysis method (software - Image Processing and Data Analysis Version 2.1 1 5), %
Sample denominations		
6h	14	17
24 hS	7	16
T36	11	12
31 SM	20	21
33M	20	20

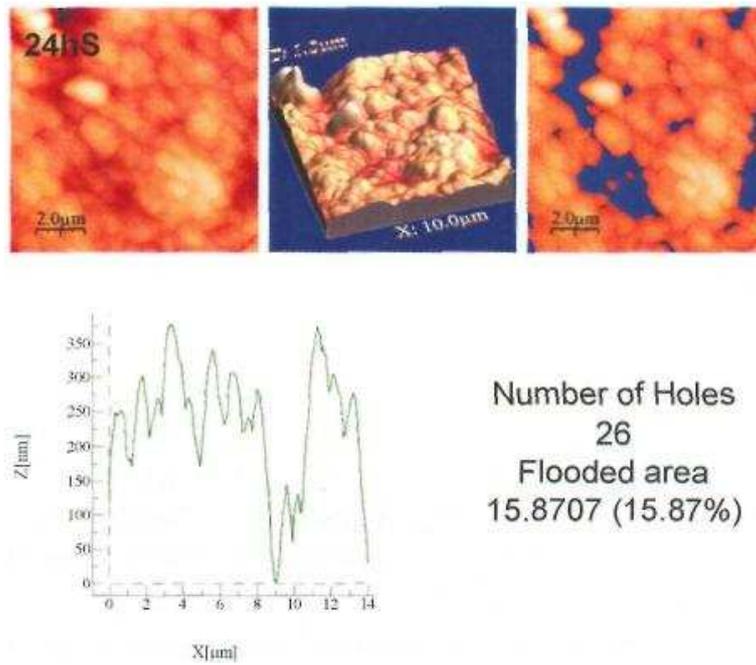


Figure 4. AFM image analysis results of 24h ceramic (1100° C)

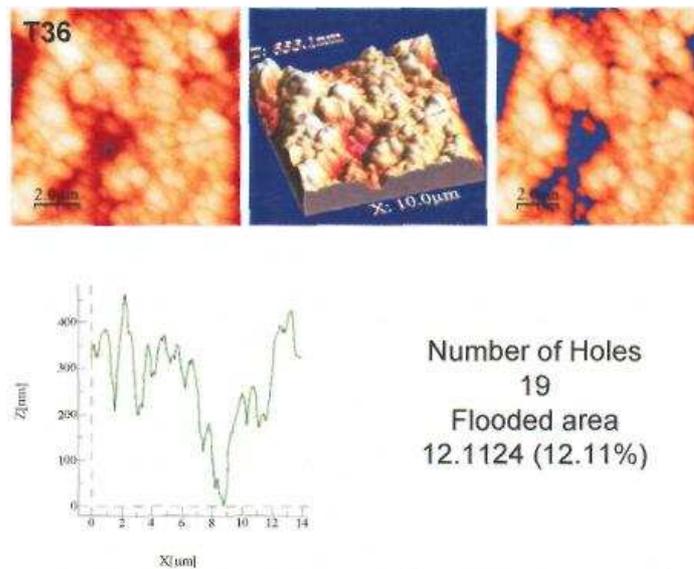


Figure 5. AFM image analysis results of T36 ceramic (1100° C)

The circumstances of hydroxylapatite ceramic sintering remarkably affect the resulting material. Ceramics with a fast thermal treatment mode (5 °C/min) has fewer macropores but it contains tricalcium phosphate phase (10 - 50 %). In the case of slow increase of the temperature (at the beginning heating rate should be 2 °C/min up to 400 - 600 C), with a very careful rising of the temperature, it is possible to ensure the formation of

HA particles in a linear configuration and simultaneously increasing the quantity of macropores.

Porosity and the apparent density were determined for the ceramics samples prepared by pressing powders with various degrees of fineness. The results show that it is possible to change the ceramics porosity by changing the size of HA grains on purpose. Denser samples were obtained from 24 h - ground (2.51 g/cm^3) and 24 hS (3.01 g/cm^3) HA powder. The relevance between the size of powder particles used for preparation of ceramics and the characteristics of porosity and density of the ceramics sintered at $1100 \text{ }^\circ\text{C}$ is almost impossible to evaluate except taking into account the range of the size of the used HA particles.

The ceramics sintered at $1100 \text{ }^\circ\text{C}$ and prepared from the finest 24hS powder has the lowest macroporosity - 7 % (see Table 4). The results of powder particle size determination by SEM state the narrow dispersion of the sizes of HA powder nanoparticles from 3 to 63 nm (Table 2). Similarly in the case of ceramics synthesized using HA prepared by the solution method and ground (6 h, 12 h, 18 h, 24 h) the size of obtained particles were within the range from 30 to 200 nm. All these samples show the increased characteristics of volume weight (more than 2.0 kg/cm^3) and the compressive strength (from 150 - 350 MPa). On the other hand, there is no sample synthesized from the mechanical chemically synthesized powders with the parameters of volume weight more than 1.7 kg/cm^3 . They also have lower compressive strength parameters and increased porosity.

Table 4

The physical and mechanical characteristics of the pressed ceramics of HA synthesized by the solution method (the results of the polished samples are in brackets)

Sample	Sample characteristics			
	Apparent porosity, %	Volume weight, g/cm^3	Compressive strength, MPa	Elasticity module, GPa
1h	21 (21)	1.49	50	0.9
6h	14(14)	1.54	180	2.8
12h	14(15)	2.21	150	2.3
18h	12(12)	2.35	150	2.3
24h	12(13)	2.51	210	3.1
24hS	7(7)	3.01	350	2.2
36h	12(13)	2.36	250	2.3
24+6h	10(14)	2.41	410	6.2

The apparent porosity was determined also for the thermally processed and then polished samples (see Table 4, where the results of the polished samples are in brackets and the polished surface was cleaned carefully from the polishing dust).

It should be noted that forming the mixtures of powders synthesized by the solution method (24+6h) it was managed to synthesize ceramics whose compressive strength reaches 410 MPa. Smaller particles have facilitated more effective packing when pressed and recrystallization processes during sintering.

Table 5

Sizes of pores of the pressed powder ceramics of HA synthesized by the mechanically chemical method and the solution method (1100° C)

Sample N°	Pore sizes of ceramics measured by SEM	Sample N°	Pore size of ceramics measured by SEM
29A	140 nm – 2.80 µm	6h	100 nm – 6.30 µm
24A	50 nm – 2.50 µm	12h	160 nm – 2.50 µm
31SM	300 nm – 12.00 µm	18h	120 nm – 4.00 µm
33	600 nm – 12.00 µm	24h	50 nm – 2.50 µm
33M	600 nm – 12.00 µm	24hS	50 nm – 1.40 µm
T36	50 nm – 2.60 µm	36h	10 nm – 2.10 µm

The obtained results convincingly point to the increased chemical activity of nanoparticles. It should be noted that passivation and agglomeration of the powders synthesized by the mechanically chemical route are possible and they could be caused by preserving synthesized HA particles for too long period before there forming and sintering.

The sizes of ceramics pores determined by the SEM analysis method are given in Table 5. Powders prepared by the mechanically chemical and the solution method are used for synthesizing ceramics. The results of SEM state that porosity changes within the range of 10 nm to 12 µm. Using HA powders synthesized by two different methods 24hS-3-63 nm (the solution method) and T36 - 3-50 nm (the mechanically chemical method) it was possible to obtain hydroxylapatite ceramics with similar pore sizes. Ceramics prepared from these powders have pore sizes within the range from 50 nm to 1.40 µm and 50 nm to 2.60 µm respectively.

As bone implants must have not only good characteristics of biocompatibility but the specific pore structure as well, the following research is devoted to usage of alcoxides in order to modify the pore structure of HA ceramics maintaining the mechanical strength.

Experimental part III: Synthesis of the sol-gel compositions.

In order to develop the porous structure in addition to the powder of HA

partially hydrolyzed $\text{TiO}_2\text{-SiO}_2$ and $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$ sols were used as the second component. The research of previous years has proved the perspective usage of the multicomponent sols of hydrolyzed alcoxides for forming a desirable pore structure [2.3]. As the results of this paper are planned to use not only forming porous ceramics but also porous coatings for titanium and its alloys, the positive influence of the oxides TiO_2 and ZrO_2 should be noted for the strengthening of the interphase between a titanium alloy and HA coating facilitating formation of chemical bonds [4]. Nanoparticles of TiO_2 can be used for bactericide aims as well [5].

Viscosity of sols is closely connected with the gelation phenomena of sols when the clusters are growing thanks to polymer condensation as the result of hydrolysis and polycondensation or aggregation of particles when clusters intergrow among themselves. The bonds form between clusters forming gigantic cluster which is called a gel. The growing gigantic cluster reaches the size of the container where it is growing and when the container is toppled the sol (more precisely - gel) cannot be poured out. At the moment of forming a gel many clusters are still in the sol phase. Uncombined clusters join the solid framework of gel and the stiffness of the gel increases with joining of clusters. According to this description a gel forms when the last bond is formed between two big clusters forming the growing gigantic cluster. This bond is responsible for the elasticity of the gel forming continuous solid framework. The viscosity of the sol depends on the circumstances of its preparation. An informative way of looking at the process of gelation is to measure the viscoelastic behaviour of the gel depending on the revolution rate of the cylinder of the viscosimeter. The aging time of sols for usage in composite materials was 10 and 22 days. As a result of the research it is stated that a 22 - day aged sol is not suitable for the preparation of composite ceramics. Adding HA powder there was not any reaction between HA and sol and that resulted in HA precipitation. Therefore for further research gels with 240 h of T_g were used. The viscosity of sols depending on the aging time is shown in Figure 6.

It can be concluded from the graph that gelation starts of about 22 days in the case of both sols. The sol loses flowness and changes into an elastic substance. SPG sol was less viscose but both sols gelled at the same time. Studying the viscosity of SG35 composition (it had two times more oxalic acid added than the composition SGE at the equal concentrations of other components) it was stated that the sol is a little more liquid-like (1d - 10.2 mPa·s and 37 d - 30.1 mPa·s), but the gel contained cracks. It can be explained that the presence of oxalic acid in the gel facilitates elimination of water during drying and it considerably

reduces the time of dehydration but its excess facilitates cracking of the samples. The composition SGP has the viscosity 29.1 mPa·s close to the T_g, but the composition SGE 33.2 mPa·s.

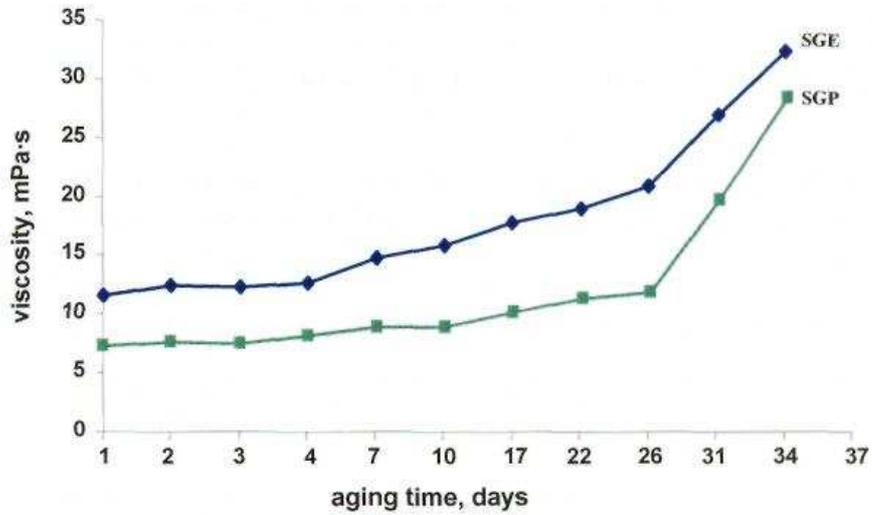


Figure 6. The viscosity of the sol depending on the aging time

Experimental part IV: Synthesis of the HA/sol composite ceramics. For preparing the composite ceramics some powders which were obtained by the mechanically chemical method were used as well as HA prepared by the solution method (24hS and 24+6).

Table 6

Samples of the HA/sols composite ceramics

Sample No	Explanation of the sample
SGE29A ₁	SGE + 29A powder in ratio 1/1
SGE29A _{0.5}	SGE + 29A powder in ratio 1/2
SGE24A ₁	SGE + 24A powder in ratio 1/1
SGE31SM ₁	SGE + 31SM powder in ratio 1/1
SGEHA ₁	SGE + HA modified 1/1
SGEHA ₁ SAS	SGEHA ₁ composition with an addition of a surface active substance (VAV*) in ratio 1/1
SGE24+6h ₁	SGE + (24+6h) HA powder in ratio 1/1
SGE24+6h ₁ SAS	SGE + (24+6h) HA powder in ratio 1/1 + SAS
SGE24hS ₁	SGE + 24hS HA powder in ratio 1/1
SGE24hS _{0.5}	SGE + 24hS HA powder in ratio 1/2
SGEHATi ₁	SGE + HA modified 1/1 + dispersed TiO ₂ addition
SGEHASi ₁	SGE + HA modified 1/1 + dispersed SiO ₂ addition
SGP24+6h _{0.25}	SGP + (24+6h) HA powder in ratio ¼
SGPHA ₁	SGE + HA modified 1/1

*SAS - Surface Active Substance

The slip gel casting mass was formed from the powders and sols, and they were poured into the forms of polymer material of the certain size. In order to improve physical and chemical properties of the composite ceramics the mixtures of HA powders (ground 24h and ground 6h in ratio 1/1) were used (Table 6). The prepared composite compositions were processed at different temperatures (100, 400, 600, 800, 1000, 1100 °C). It can be concluded from the results of RTg that up to 1000 °C in the samples SGE29A₁, SGE24A₁, SGE31SM₁, SGE24h₁ there exists only the phase of hydroxylapatite but at the temperature 1100 °C the crystalline phase of tricalcium phosphate appears. In a case of the composition SGEHA₁ hydroxyapatite remains to 1000 °C but at higher temperatures calcium orthosilicate (CaSiO₃) forms as an additional phase as well as anatase and low-temperature quartz. For the sample SGEHATi₁ at the temperature higher than 1000 °C in addition to hydroxylapatite forms the crystalline phase of anatase, for SGEHASi₁ - forms high-temperature quartz, but for SGP_{HA}₁ and SGP24 + 6h_{0,25} samples forms baddeleyte.

Only some compositions from many initial compositions for composite ceramics were chosen for further research, the others were dropped for several reasons. They developed cracks during drying and sintering or they crumbled. Some ceramic compositions crumbled immediately after drying, some during the sintering.

The results of thermogravimetric analysis state that the total mass loss of composite materials is 24 %. Considerable mass losses were observed within the whole temperature range subjecting the samples to the influence of the temperature from the room temperature to 800 °C, and they are connected with dehydration and removal of the adsorbed water or organic compounds. The exothermic maximums are characteristic for this temperature interval and they are connected with the restructurization of the crystalline lattice (for the composition SGE it is anatase, but for SGP baddeleyte is forming), removal of the water present in the structure, as well as the oxidation process of the alcohols and highmolecular hydrocarbons. The maximums on the DTA runs of the composition of SGE at 890-900 °C and 1000-1120 °C refer to the anatase, quartz and calcium orthosilicate crystalline phase formation processes.

The microstructure of the pores and their walls can be controlled by changing the concentration of the additives, amount of HA in compositions, by the use of various solvents, etc. In cases of the laminate type HA porous ceramics development using organic additives it is

possible to obtain a good density of pores with suitable sizes in the outer layer and the layer combining during the shrinkage process [5].

The results of optical microscopy state that the prepared samples of the composite ceramics have a developed structure of pores; the maximal size of the pores achieves more than 1000 urn (see Figure 7). The formation of the pores is connected with the components formed by sol-gel process and evaporation of the water and the solvent from this component, decomposition of the organic part and oxidation during the samples thermal processing.

Using sol-gel technology an interconnected pore structure is obtained. Mixing HA powders with sols the obtained porosity for composite materials does not exceed 60 % (53-60 %). At such a porosity the compressive strength is 5-20 MPa (Table 7), the density 1.44 - 1.50 g/cm³, and these results coincide with commercially available porous HA ceramics.

Mixing modified HA with systems TiO₂-SiO₂-ZrO₂ and TiO₂-SiO₂ sols a porous HA ceramics with a porosity 34 - 40 % is obtained. The density of this ceramics is 1.54 - 2.87 g/cm³ but the compressive strength reaches up to 730 MPa.

The systems with an addition of the surface active substances were tried in the research. The porosity results (also for polished samples) are shown in Table 7. Porosity is higher about 2-6 % in all the samples with surface active substances than in the samples without it, except for the composition SGE31SM₁(57 %).

The images made using optical microscopy for the samples of the composite ceramics are shown in figure 7.

Using surface active substances for the preparation of composite ceramics it is possible to achieve more even distribution of particles and pores. Ceramics prepared from the powders 29A, 31SM, and 24A with the composition of SGE sol is mechanically fragile and crumbles easily therefore it is not suitable for preparing for actually used materials. Using nanosized powders 24+6h and 24hS ceramics is denser and mechanically harder, nevertheless, the strength results are not high. The sample SGE24hS was comparatively harder mechanically but a lot of cracks can be seen in the figure which obviously form due to high surface tension.

Using milled powder prepared by the solution method for preparation of ceramics the samples do not form cracks if equal proportions of the components are used for preparing composite ceramics. The compressive strength is as low as for the ceramics prepared from the mechanically chemically obtained powder. When creating a material with other proportions of the components, the samples form cracks even during

the process of drying, and they crumble. It was possible to increase the strength characteristics considerably using the powder 24+6h with the SGP sol composition; the compressive strength in this case is 730 MPa.

Table 7

Characteristics of the composite HA/sol ceramics (porosity results of the polished samples are given in brackets)

Sample	Sample characteristics			
	Apparent porosity, %	Volume weight, g/cm ³	Compressive strength, MPa	Elasticity module, GPa
SGE29A ₁	47 (47)	1.44	10	2.3
SGE29A ₁ SAS	60 (60)	1.34	20	2.9
SGE24A ₁	59 (60)	1.49	20	1.9
SGE31SM ₁	57 (57)	1.50	10	2.0
SGEHA ₁	40 (40)	1.67	180	1.3
SGE24hS ₁	59 (59)	1.48	5	0.7
SGE24+6h ₁	49 (50)	1.47	10	1.1
SGE24+6h ₁ SAS	53 (54)	1.77	10	2.1
SGEHATi ₁	57 (57)	2.70	320	3.5
SGEHASi ₁	58 (59)	2.74	250	4.9
SGP24+6h _{0.25}	34 (34)	2.87	730	14.3

Cracks form in the ceramics SGE29A₁ during drying, but for the same composition with added SAS (SGE29A₁SAS) the distribution of pores is very even, porosity increases to 13 % (Table 7), nevertheless, strength parameters do not improve much (from 10 to 20 MPa).

The images acquired with the help of optical microscopy (Table 7) show that in case of composite compositions SGEHASi₁, SGEHATi₁, SGP24+6h_{0.25} diameter of pores is around 1000 micrometres. Ceramics prepared from the modified HA does not show a considerable increase of porosity results (difference 2-8 %) with and without SAS.

The AFM has several advantages compared to the SEM because the latter gives the 2D projection of the sample, but the AFM gives a truthful 3D image of the topography of surface.

The results of the topographical analysis of AFM state the presence of a connected net of pores. The presence of the connected net of pores in the samples of composite HA ceramics is also confirmed by apparent porosity results determined by the traditional method of detecting pores (see Table 2, Figures 8, 9).

The powder particles obtained from HA with the solution method form chainlike structures in the sol gel derived matrix during the process of synthesis. It can be seen well in the composite materials prepared from

the SGE sol composition and the mixture of particles 24+6h, as well as for the identical composition with an addition of SAS.

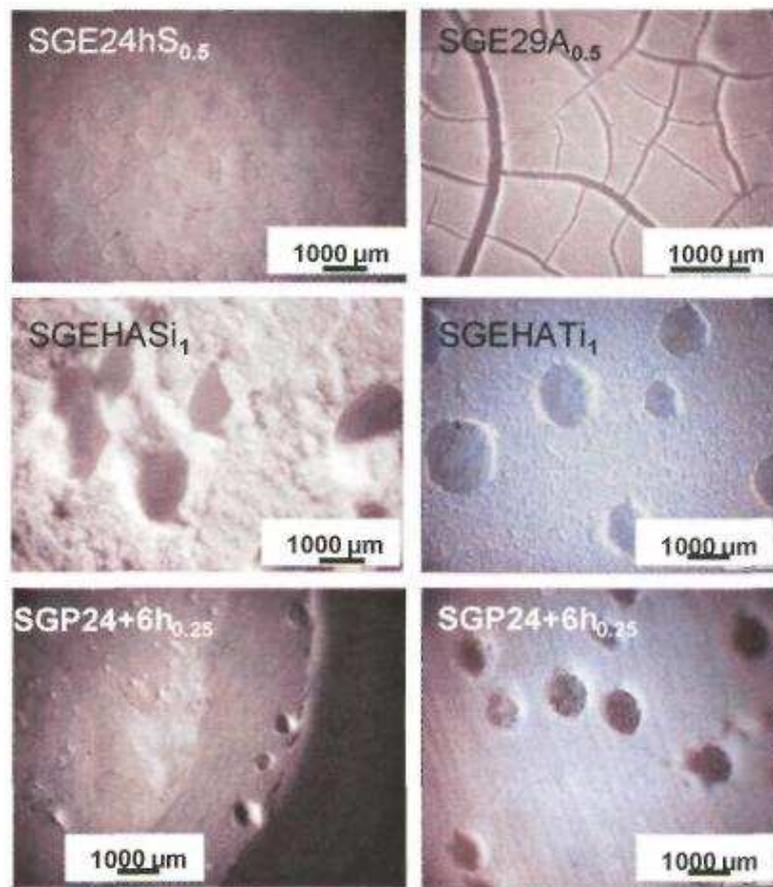


Figure 7. Optical microscopy micrographs of the composites $SGE24hS_{0.5}$, $SGE29AS_{0.5}$, $SGEHASi_1$, $SGEHATi_1$, $SGP24+6h_{0.25}$ (the surface of the sample) and $SGP24+6h_{0.25}$ (cross section)



Figure 8. AFM results of the surface topography analysis of composite ceramic $SGE24+6h_{ISAS}$

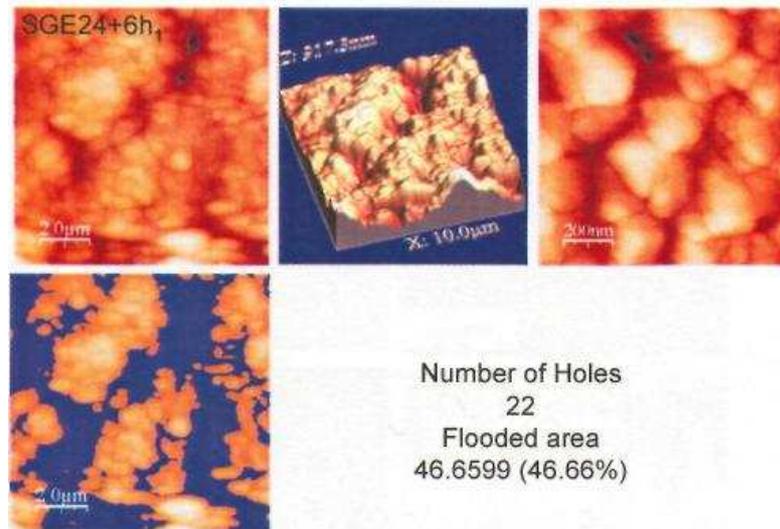


Figure 9. AFM results of the surface topography analysis of composite ceramic SGE24+6h₁

The data of SEM prove that it is possible to obtain a larger size of pores in the ceramics prepared using the sol-gel matrixes than in HA ceramics prepared from HA nanopowders by dry pressing (Figure 10).

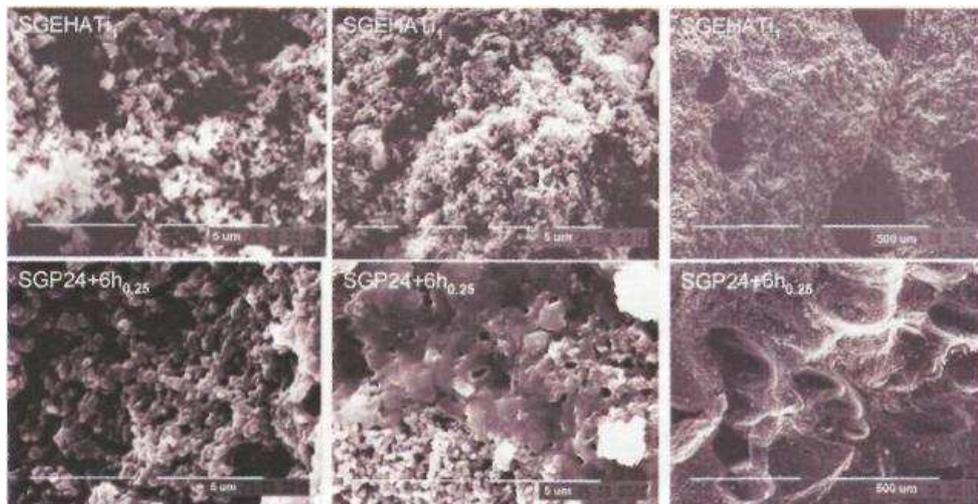


Figure 10. SEM microphotographies of composites SGE24h_{0.5}, SGE29AS₁, SGE24+6h_{0.5}, SGE24hS₁

As the previous research shows (Research performed by the Association of Latvia Waste Product Management), the sorption of heavy metals with the help of yeast cultures is a complex process which is determined by several parameters including ions of heavy metals and their

concentration, environment pH, the presence of other ions, a kind of biosorbent, as well as technological aspects of the sorption process.

Studies that have been done so far give the basis for successful application of biosorbents of yeast cultures in cleaning industrial waste waters polluted with heavy metals (including concentrated waste waters) [6].

Experimental studies of immobilization of yeast cells on the surface of HA and waste-water cleaning is performed in the solutions of different pH, therefore it was necessary to check the chemical stability of the obtained HA ceramics.

Pressed ceramics prepared from powders T36, 33M, 31SM and 6h, 24h (Figure 11), 24hS and 24+6h showed almost identical results of chemical durability except for the ceramics 29A. The chosen solutions for studies were pH2 (HCl), pH4 (HCl), pH6 (H₂O_{dest}) and pH8 (NaOH). Pressed platelets (5 platelets per 100 ml of a solution) were immersed in the solutions of different pH for 1h, 4h and 24h (static mode) or stirred during 1h using a magnetic stirrer (dynamic mode).

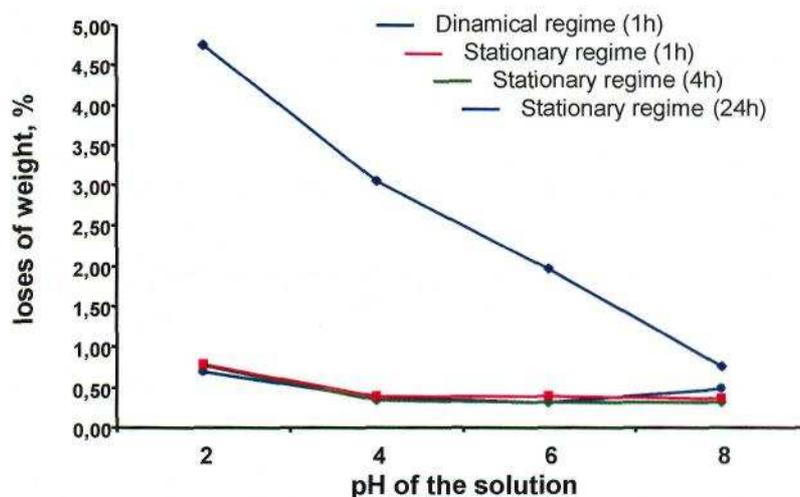


Figure 11. Results of chemical durability (24h) of ceramic samples in different pH media.

The results showed that the ceramics mass losses ($\Delta m_{\text{average}}$) reaches 15 mass % at pH2. The samples have relatively high chemical durability - $\Delta_{\text{average}} = 0.4$ mass % in the solutions of pH 6 and pH 8.

The results of chemical durability of the samples in the dynamic mode are not supposed to be an example for actual chemical durability in

various pH due to mechanical interaction among samples (collisions between the platelets during rotation); mechanical degradation takes place.

There is no mechanical influence in the static mode therefore the results of chemical endurance are similar for the samples made by pressing and sintering of powders synthesized mechanically and chemically and HA powders synthesized by the solution method.

The samples of composite ceramics prepared from the compositions SGE and SGP sol-gel in the mixture with HA are exceptions. It should be noted that in the cases of the compositions SGEHASi₁, SGEHATi₁ and SGP24+6h_{0,25} the used HA powder was synthesized by the solution method. They showed good chemical durability in the dynamic mode (SGEHASi₁, SGEHATi₁, SGP24+6h_{0,25} 0.8, 0.7, and 0.4 % accordingly) and excellent results of chemical durability in the stationary mode (0.1, 0 and 0 %).

The possible areas of application of hydroxylapatite ceramics and some properties connected with them. The prepared ceramics is expected to be widely applied in medicine, food industry, and technologies for cleaning the environment. So it is necessary to adjust the ceramics parameters to the specific type of cells and microorganisms which determine not only the methodology of solving biological experiments but also the connected properties of the surface of the material.

Preparation of suitable HA material for several possible application spheres of HA ceramics is connected not only with fabrication of hydroxylapatite nanopowder and sintering of ceramics which controls the volume and the size of pores, but also with the possibilities of modifying the surface of HA ceramics which are tended for guaranteeing specific properties and parameters. The controlled change of physical and chemical properties, the biological compatibility of the obtained ceramics samples, evaluation of cell immobilization and functioning on the porous surface of HA material is connected with the studies of parameters of different kinds of biologically active compositions of the porous ceramics and modifications.

The studies carried out during the recent months demonstrated that hydroxylapatite has specific properties of the surface which ensure additional stimulation of interaction between HA and live cells. The characteristics of biological compatibility of HA ceramics can be increased, if it is possible to ensure a certain charge on its surface [7].

The polarization mechanism, the changes of the electrical charge on HA surface, mechanical and adhesive properties are still unexplained.

The polarization of HA surface takes place when a charged proton H^+ moves into the components of HA nanostructure. The process has an electret character as it is influenced by the electric field and temperature. It has been established that by changing the state of the volume of HA material and surface charging, it is possible to achieve different wetting angles of the same HA material.

The ability to receive the electrical charge is stated to be dependent on the porosity of the ceramics. The charged surface of the porous ceramics demonstrates an uneven distribution of the charge. The accumulation of the charge is connected with vacancies of OH^- .

The results of the experiments indicate two main factors which determine the ability of the cells to stick to the surface, that is, porosity of the surface and the surface charge due to oriented charging. The first parameter, porosity, should ensure places on the ceramics surfaces with pore sizes which are suitable for cell receptors. Additionally the pores form a net of canals which facilitates the changing of metabolites around the connected cell. The charging of the surface guarantees an additional stimulus for the cells influencing cell receptors and a membrane with an electrical field, thus stimulating cells to cluster on the ceramics surface.

Thermostimulation of the emission of ekzoelectrons of hydroxylapatite bioceramics nanostructures and luminescence in the wide range of temperatures is an effective method used in spectroscopy.



Figure 12. Different wettability states of hydroxyapatite bioceramics: a) the sample subjected to electron irradiation with $We=100$ eV; b) the annealed sample; c) as-prepared (nonirradiated) sample [7]

As a result of the studies a method has been found which is based on the change of volume of HA ceramics and the state of surface electrons, therefore modifying the wetting properties of HA (Figure 12).

The series of HA samples was subjected to electron radiation using an increased time span and studying the wetting angle of the ceramics from $Q=0^\circ$ to $Q=100^\circ$. The influence of wetting angles can be seen in Figure 13 where difference of sticking of biological molecules depends on the degree of hydrophobicity of the surface. In such a way deoxiribonucleus acid (DNA is a very hydrophil molecule) moves to the

surface which has a bigger wetting angle (Figure 13, the top). On the other hand, a good connection of HA surface and the bone serum albumin (protein BSA) has been stated (Figure 13, the bottom) where BSA can be seen enjoining hydrophobic spheres.

The achieved experimental results can be used as a basis for forming biologically active components which will guarantee an increased productivity of bioreactors in food industry, pharmaceutical technologies and technologies for cleaning the environment (mainly the sorption of heavy metals). Using of macro and microporous ceramics materials in medicine for production of implants is connected with the improved implant material and the possibility to increase the level of biocompatibility.

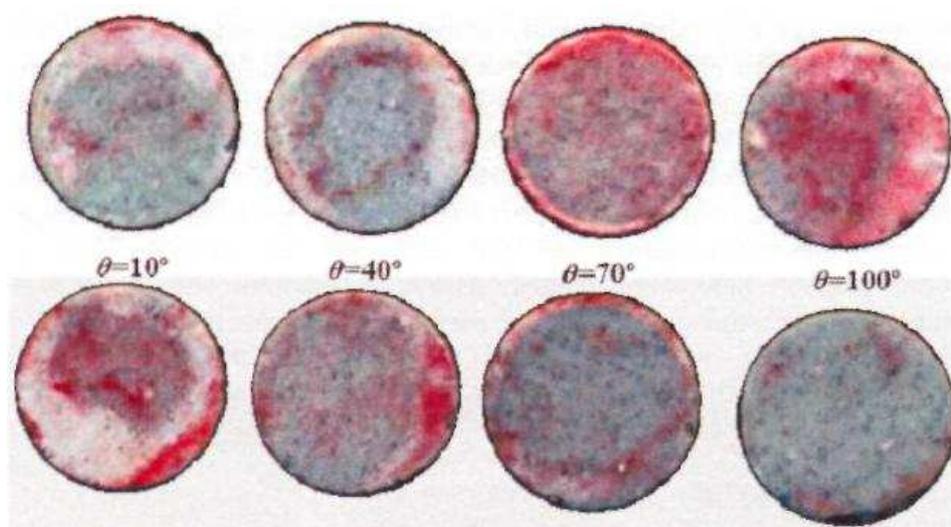


Figure 13. Adhesion of bovine serum albumin (BSA) (upper row) and DNA (lower row) to Hydroxy apatite surfaces with different wettability state. (θ is the contact angle). The ceramic samples were Giemsa stained and the biomolecules were stained in red [7]

Conclusions.

Hydroxylapatite powder has been synthesized by the solution method, and the powder has only one crystalline phase, that is, hydroxylapatite. Grinding the prepared powder in a planetary mill will give the possibility to achieve nanosized hydroxylapatite powders whose particle size is within the range of 300 nm to 10.00 μm (6h), 50 nm - 200 nm (12h), 50 nm - 150 nm (18h), 30 nm - 100 nm (24h), 3 nm - 63 nm (24hS) and 30 nm - 900 nm (36h). By sieving of the powder it was possible to separate larger particles and achieve the particles within the

size of 3-63 nm. The observed phenomenon states the adsorption of nanoparticles on HA particles of microsize.

By pressing the ceramics from the powder which was prepared by the solution method, the compressive strength of the obtained material increases while the apparent porosity decreases: 6h - the apparent porosity (V_a) is 14 % and the compressive strength is (σ) — 180 MPa, for the ceramics pressed from 24 - hour ground powder - $V_a = 12$ % and $\sigma - 200$ MPa. Increased characteristics of strength ($V_a = 7$ % and $\sigma - 350$ MPa) can be achieved by pressing the ceramics from sieved powder and also using the powder where 50 mass % consist of 24 - hour ground powder (30 nm - 100 nm) and 50 mass % consist of 6 - hour ground one (300 nm - 10.00 μm) for pressing the ceramics as well ($V_a = 12\%$ and $\sigma - 410$ MPa).

The ceramics which was obtained by pressing the mechanically chemically synthesized powders has low strength characteristics: the ceramics 29A (particle size 100 nm - 5.50 μm) $V_a =$ (%) and $\sigma - 90$ MPa, 31SM (particle size 500 nm - 1.00 μm) $V_a = 20$ % and $\sigma - 20$ MPa, 24A (particle size 800 nm - 12.00 μm) $V_a = 14$ % and $\sigma - 200$ MPa, T36 (particle size 3 nm - 50 nm) $V_a = 11$ % and $\sigma - 130$ MPa. The observed phenomenon may be connected with transformation of nanosize powder particles under the influence of the environment.

Sol-gel compositions upon the basis of the systems $\text{TiO}_2\text{-SiO}_2/\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$ have been worked out and chosen for preparation of the composite ceramics. It has been established that the most optimal time of sols application is 240 h, at that time the viscosity of $\text{TiO}_2\text{-SiO}_2$ sol and $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$ sol is 16.2 mPa·s and 9 mPa·s, respectively. The stated relationship is connected with the sizes the formed polymer $\text{TiO}_2\text{-SiO}_2$ and $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$ in compounds in the sol and the reaction ability of OH⁻ groups of HA powder. Adding HA powder at a lower sol viscosity the spontaneous gelation of the sol takes place, but above 16.2mPa·s and 9mPa·s HA and the sol exist as separate phases.

Using partly hydrolyzed solutions and HA nanopowders synthesized by different methods for preparing composite ceramics the composite ceramics with excellent parameters of porosity and compressive strength has been obtained: SGEHATi₁ - $V_a = 57$ %, $\sigma - 320$ MPa, SGEHASi₁ - $V_a = 58$ %, $\sigma - 250$ MPa and SGP24+6h_{0.25} - $V_a = 34$ %, $\sigma - 730$ MPa.

Studies connected with the addition of surface active substances confirmed usefulness of their usage forming more even structure of pore division, providing the supposed porosity 13 % higher, and practically not influencing the strength parameters $\sigma - 10$ MPa.

During the studies it has been established that the mode of drying and sintering considerably influences the structure and properties of composite ceramics. It is proved by studies of Rtg analysis (mainly tricalcium phosphate forms for fast-sintered ceramics). AFM studies show that the ceramics with a fast sintering mode (5 °C/min) has less rough surface, but larger particle sizes. On the other hand, a slow sintering mode (2 °C/min) with a slow increase of burning temperature at the beginning to 400 - 600 °C guarantees the possibility to obtain HA ceramics with nanosize particles of hydroxylapatite. It is obvious that the process is connected with successful recrystallization of the secondary HA during the case of low heating, therefore ensuring suitability of the ceramic structure with the crystalline phase of hydroxylapatite.

High results of chemical durability in various pH media (pH2, pH4, pH6 and pH8) in the stationary and the dynamic mode have been achieved for the ceramics obtained by using partially hydrolyzed alcoxide solutions, for example, SGEHASi₁, SGEHATi₁, SGP24+6h_{0.25} the mass losses is 0.8, 0.7 and 0.4 % in the dynamic mode and 0.1, 0 and 0 % in the stationary mode. On the other hand, the results of chemical durability of the ceramics pressed from the powder were for 29A: 15 % in the dynamic mode and 3.5 % in the stationary mode and for 24hS: 6.2 % in the dynamic mode and 1.7 % in the stationary mode.

In case of composite ceramics it is possible to achieve up to 38 times higher parameters of chemical durability in various pH media both in the stationary and the dynamic mode of chemical durability determination. The stated relationship is connected both with the increased parameters of strength characteristics (in case of the dynamic chemical endurance) and with the increased stability of the matrix formed by sol-gel.

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