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Composites Hydroxyapatite with Addition of Zirconium Phase

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1. Indroduction

Osteoporosis is a disease in which the density and quality of bone are reduced, leading to weakness of the skeleton and increased risk of fracture. Osteoporosis literally means "porous bone". When a bone has become osteoporotic or osteopenic (low bone mass), the risk of a fracture increases. The forearm, spine and hip are the most common fracture sites, accounting for more than 80 percent of all fractures. Osteoporosis and associated fractures are an important cause of mortality and morbidity. 20 percent of hip fractures lead to death within a year. Osteoporosis is a widespread public health problem. The costs to national healthcare systems from osteoporosis-related hospitalization are staggering. In the US, the cost to the health care system associated with osteoporotic fractures is approximately $17 billion annually. This converts to more than $45 million a day! Each hip fracture represents an estimated $40,000 in total medical costs.

Human skeleton makes up a load-bearing structure for motor organs and it constitutes a location for attachment of tendons and ligaments. Mature bone has a lamellar structure with layers and comprises compact (cortical) bone and trabecular (spongy) bone. Cortical layer consists of cylindrically arranged lamellae, while spongy bone is composed of threedimensional, irregular trabeculae in the form of a network. Space between trabeculae is filled with hematopoietic system cells and adipose tissue (Fig. 1). Matrix of the bone consists of organic compounds called osseine, which is responsible for bone elasticity as well as of mineral compounds: magnesium phosphate, calcium carbonate and calcium hydroxyapatite, which provide bones a particular hardness. Deviation from proper level of minerals in relation to organic compounds might cause lack of bone elasticity, thus its brittleness. Main mineral compound of bones is *calcium hydroxyapatite* with crystal size that ranges from 4-50 nm. Hydroxyapatite is a 'warehouse' for the most of calcium (99%) and phosphorus (85%) contained within the body. Hydroxyapatite crystals account to as much as 77% of organic stroma the bones are composed of (Fig. 1).

Moreover, hydroxyapatite is the main mineral component of dentine (Fig. 2). Dentine comprises essential part of the mass of hard tissues, which human teeth are made of. In the area of the crown, the dentine is covered with enamel, while in the area of the root – with cementum. Teeth (singular: tooth) are dense structures found in the jaws of many

vertebrates. They have various structures to allow them to fulfill their different purposes. The primary function of teeth is to tear, smell and chew food, while for carnivores it is also a weapon. Therefore, teeth have to withstand a range of physical and chemical processes, including compressive forces (up to ~ 700 N), abrasion and chemical attack due to acidic foods or products of bacterial metabolism.

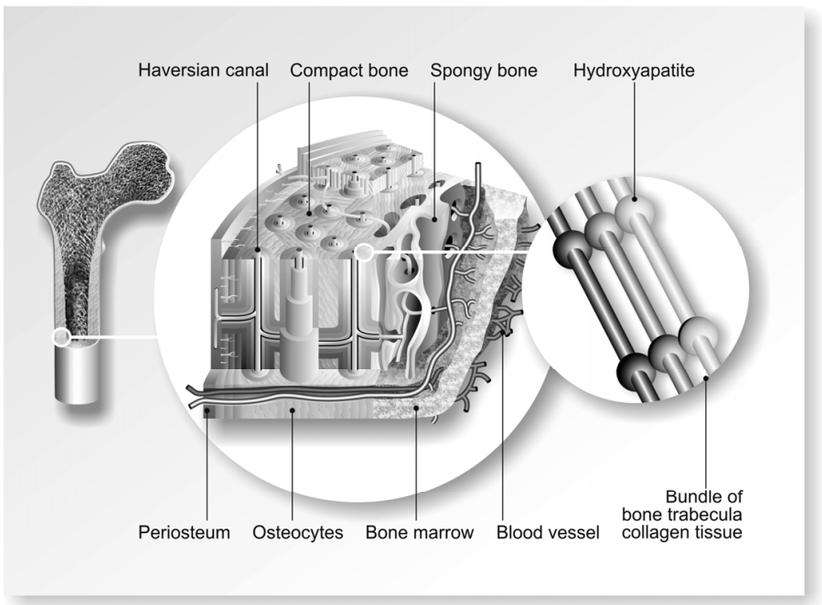

Fig. 1. Section of a bone

Nowadays dentists, in their practice, often encounter problems of bone defects which occur as a result of removal of bone cyst or through alveolar process artophy. Bone graft is a standard procedure during treatment of such defects. The locations from which transplants are taken include: mentum (area next to canines), cranial vault and iliac ala. This methodology has some advantages, e.g. no graft rejection reaction, however, its fundamental drawback is the fact that this requires additional surgical intervention, which might lead to some disorders in the location the grafts are taken from.

Due to the abovementioned facts, a great emphasis is on searching for bone-replacing materials which would allow for filling of bone defects resulting from a variety of reasons. Such materials would eliminate many complications which occur during use of materials of autogenic [1], allogenic[2] or xenogenic [3] origins.

Development of materials for medicine applications was first recorded in 1860, when doctor J. Lister developed aseptic techniques used in surgery. Previous attempts with use of biomaterials frequently ended up with infections spreading throughout the patients' bodies, thus causing demise. Since then, further developments started to spread rapidly. Some discoveries were made almost 'by the way', e.g. during the Second World War lack of

[1]Graft from the same body
[2]Material for the graft taken from a specimen of the same species, genetically different than recipient
[3]Graft taken from a specimen of different species

chronic adverse reactions was observed in wounded pilots as some parts of aircraft canopies, made of polymethyl methacrylate, were left lodged in their bodies for a longer time. Nowadays, this material is widely used, e.g. it replaces parts of skull bones.

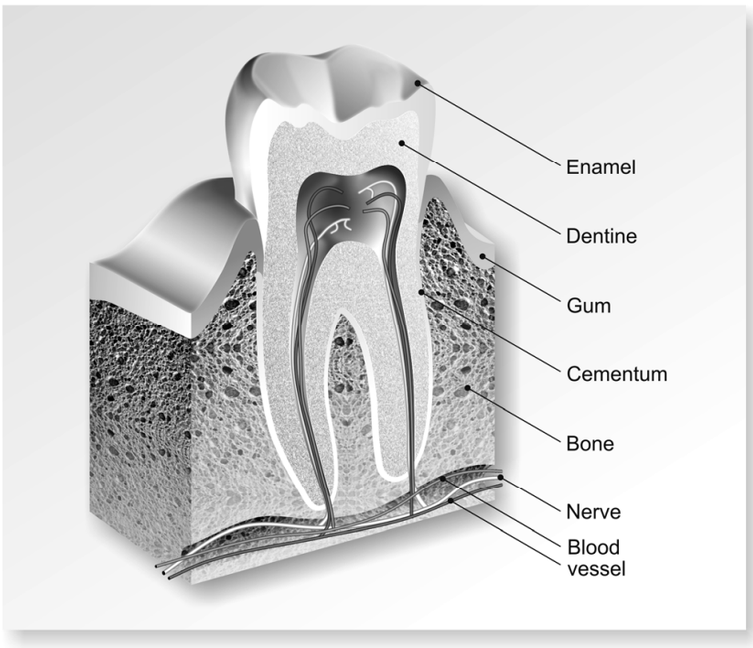

Fig. 2. Section of a tooth

2. Material for Implants – Biomaterials

According to the definition adopted by the European Society for Biomaterials, biomaterials include the compounds which are not medicines or combination of natural and synthetic substances, and, which might replace a part or the whole tissue or organ.

Materials that implants are made of [4] must not be hazardous for human body, i.e. carcinogenic, toxic or radioactive, they have to be resistant to corrosion (depending on the environment they work within), biocompatible (the materials which show tissue compatibility and do not trigger allergic reactions), well tolerated by living tissues. Implant acquire their fundamental properties and biocompatibility through specific chemical constitution of a material it is made of. It is characterized by biotolerance, .i.e. biological compatibility and harmony of interaction with living matter. Biotolerance causes that an implant, having been implemented into the body, does not trigger acute or chronic reactions or inflammatory condition in adjacent tissues. The biggest importance for implant acceptance by a tissue and for the process of osseointegration is the composition of its surface layer. Another important issue is osteointegration[5], i.e. ingrowth of bone tissue into the implant surface, and, in consequence, integration of the graft with the bone.

[4]Medical devices made of one or more biomaterials which might be located in the body, partly or entirely under the skin

[5]Osteointegration - ingrowth of living bone tissue into the titanium implant surface

Biomaterials are used, among other things, in orthopaedics, cardiology, nanosurgery and dentistry (Fig. 3).

There are several groups of materials which have been used and which replace steels and temporarily damaged or ill organs or their parts (Fig. 4).

Analysis of clinical experience in terms of human body reactions to metallic implants allows to emphasise the following complications:

- immunological oversensitivity, which contributes to bone necrosis or soft tissue necrosis,
- thrombuses,
- risk of immediate and subsequent infections,
- reduction in cells' resistance to bacteria, resulting from reduction of pH factor near the graft,
- weakening of neutrophiles and macrophages that facilitate development of bacterial flora, caused by electrical potential gradient at the interface of metal – body fluid.

Lack of metallic biomaterial which are entirely neutral to human body causes that research works toward searching, improvement and modification of such materials are a necessity.

One of the suggestions for improvement of biotolerance in applied metallic materials is the use of ceramic coatings.

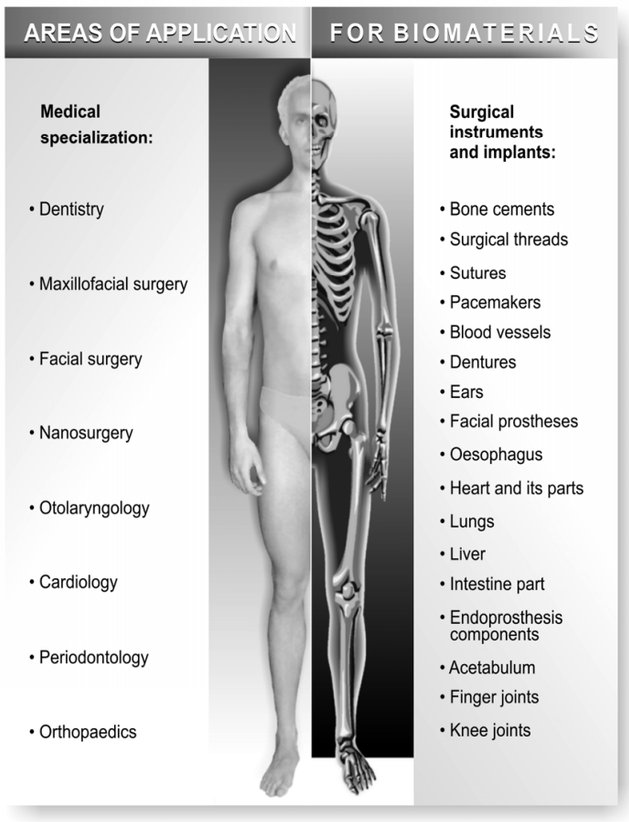

Fig. 3. Areas of application for biomaterials

Fig. 4. Comparison of biomaterials and areas of their application

Bioceramics, despite their high hardness and, in consequence, higher brittleness, have an essential advantage i.e. their porosity, which ensures integration of vascularised soft tissue, which, in effect, becomes a permanent connection. Good adhesion of the material grafted into the bone is a very important problem of implantology. There have been attempts to solve this problem through application of bioactive ceramics which 'spontaneously' connects with the bone.

Ensuring effective biological connection of ceramics (composite) with the bone depends on pores size and their spatial distribution, i.e.:

- pores over 5μm – no tissue ingrowing occurs,
- over 25μm – ingrowing of fibrous tissue and vessels,
- over 50μm – mineralization of ingrown pores,
- over 75μm – mineralization occurs at the depth of 500μm,
- większe od 100μm – mineralization occurs even at the depth of over 1000μm, ensuring proper bone formation.

According to many authors, the most optimal pore size maintains at the level of 100-500μm.

Phase and chemical composition of bioactive materials is selected so as to ensure that implant surface adjacent to tissue or body fluids constitutes an intermediate layer which connects an implant with bone tissue. A variety of materials which fulfil such criteria have been developed in recent years. The most frequently used bioceramics, due to their high mechanical, corrosion and wear resistance as well as their non-toxicity and biocompatibility, include oxides: Al_2O_3 (whose use for medicine is dated back to the thirties of the past century), ZrO_2 and calcium phosphates (Tab. 1, 2).

Symbol	Chemical formula	Name	Ca/P - - Atoms relation
DCPD	$CaHPO_4\ 2H_2O$	Dicalcium phosphate dihydrate	1.00
DCPA	$CaHPO_4$	Dicalcium phosphate anhydrous	1.00
OCP	$CaH(PO_4)_3\ 2{,}5\ H_2O$	Octacalcium phosphate	1.33
TCP	$Ca_3(PO_4)_2$-α $Ca_3(PO_4)_2$-β	α - Tricalcium phosphate β - Tricalcium phosphate	1.50
HA	$Ca_{10}(PO_4)_6(OH)_2$	Hydroxyapatite	1.67
TTCP	$Ca_4(PO_4)_2O$	Tetracalcium phosphate	2.00

Table 1. Comparison of calcium phosphates existing at the temperature of 25^0C

	Human bone	Ti-6Al-4V	Al_2O_3	HAp	ZrO_2
ρ [g cm^{-3}]	1.99	4.5	> 3.9	3.16-3.23	6.0
YS [MPa]	200	884	4000	509-917	-
TS [MPa]	130	940	-	-	> 650
E [GPa]	18-19	113	380	4.0-117	210
Porosity [%]	80	-	-	-	-
Microhardness HV [MPa]	-	260	2300	343	1200

Table 2. Properties of human bone and comparison with selected materials

Calcium orthophosphates are chemical compounds of special interest in many interdisciplinary fields of science, including geology, chemistry, biology and medicine. The main driving force behind the use of calcium orthophosphates as bone substitute materials is their chemical similarity to the mineral component of mammalian bones and teeth

calcium orthophosphates are also known to be osteoconductive (able to provide a scaffold or template for new bone formation).the major limitations to use calcium orthophosphates as load-bearing bioceramics are their mechanical properties; namely, they are brittle with a poor fatigue resistance. In general, calcium orthophosphate bioceramics should be characterized from many viewpoints such as the chemical composition (stoichiometry and purity), homogeneity, phase distribution, morphology, grain sizes and shape, grain boundaries, crystallite size, crystallinity, pores, cracks, surface, *etc*. From the chemical point of view, the vast majority of calcium orthophosphate bioceramics is based on HA, β-TCP, α-TCP.

A sintering procedure appears to be of a great importance to manufacture bulk bioceramics with the required properties. Usually, this stage is carried out according to controlled temperature programs of electric furnaces in adjusted ambience of air with necessary additional gasses; however, always at temperatures below the melting points of the materials. The heating rate, sintering temperature and holding time depend on the starting materials. For example, in the case of HA, these values are in the ranges of 0.5–3 °C/min, 1000–1250 °C and 2–5 h, respectively. In the majority cases, sintering allows a structure to retain its shape. However, this process might be accompanied by a considerable degree of shrinkage, which must be accommodated in the fabrication process.

Hydroxyapatite (HA, HAp), with formula of $Ca_{10}(PO_4)_6(OH)_2$, is a compound which is chemically and mineralogically similar to inorganic substances from which human bone tissue, including teeth, is made of. Hydroxyapatite crystallizes stechiometrically in monoclinic system, while synthetic, mineralogical and biological one shows hexagonal structure (Fig. 5). In its chemical constitution, HA contains 1.8% of H_2O. While heated, HA is stabile until 1703K, then it irreversibly looses hydroxyl groups, gradually changing into oxyapatite $Ca_{10}(PO_4)_6O$. At 1503K it might lose as much as 75% of water, maintaining its apatite structure.

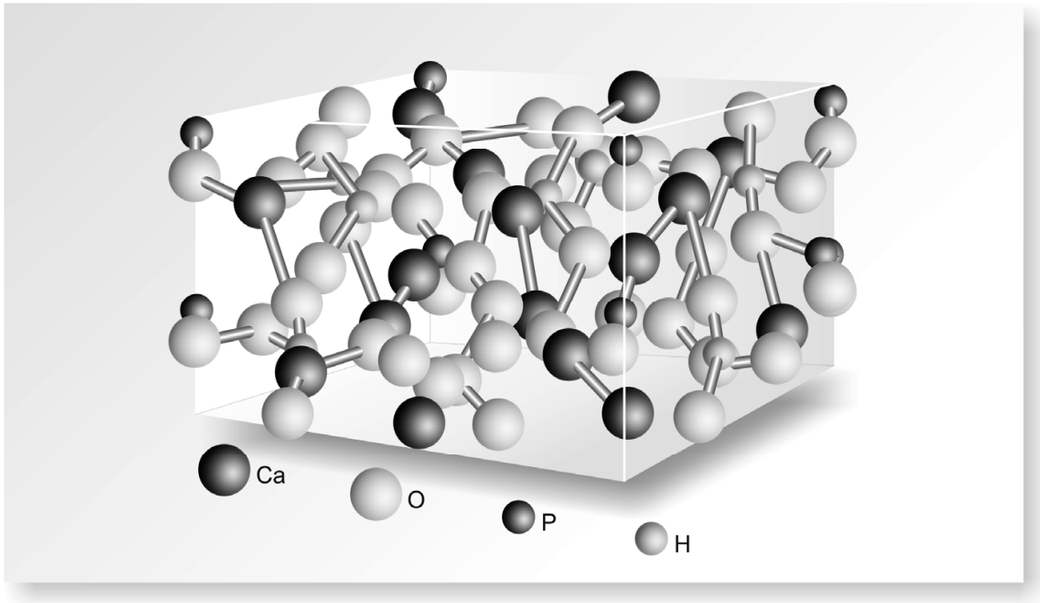

Fig. 5. Crystallographic structure of hydroxyapatite

Hydroxyapatite material is osteoconductive[6] and, on smaller scale, osteoinductive, thus implants made of this material can be directly integrated with the bone. After implantation of the material, osteogenesis[7] occurs and the layer which connects the surface of the hydroxyapatite graft with bone tissue appears. HA is a material which is characterized with small biodegradation rate – resorption in the body amounts to from 5 to 15% yearly. The process of connection of implant with the bone takes ca. a year.

Application of phosphate-calcium ceramics for implantology depend mainly, in terms of their bioactivity, on their:

1. porosity,
2. chemical and phase composition,
3. crystallinity degree.

Hydroxyapatite ceramics have been successfully used in dentistry, facial surgery, orthopaedics and otolaryngology in the form of shaped pieces and porous granules for replenishment of bone defects in the locations which do not bear mechanical load (e.g. malleus). Wider use of this ceramics, despite their best bioactivity and biocompatibility, is limited due to their poor mechanical properties.

The researchers have frequently attempted to improve mechanical strength and resistance to cracking through introduction of ZrO_2, Y_2O_3 and CaO oxides into HA. Zirconium oxide, commonly used for production of femoral joint prostheses, while its impact on composite reinforcement is determined, among other things, by stress distribution in material during polymorphous t↔m (tetragonal to monoclinic) transition of ZrO_2 during martensite transition.

Thus it seems to be necessary to strive for development of a composite with HAp matrix, while reinforcing phase should consist of other materials well-tolerated by living tissues.

3. HA+ZrO_2 ceramic composites

From the standpoint of common use of hydroxyapatite and HAp-based composites (with addition of ZrO_2 phase) for medicine, it is very important to determine such percentage content of ZrO_2 phase addition in the mixture that invariable or predictable dimensions of an implant or coating are maintained after the process of sintering.

The goal of the investigations: The investigations aimed to determine thermal stability in hydroxyapatite and HAp + ZrO_2 composites and the impact of 8%wt. and 20%wt. Y_2O_3 additions of ZrO_2 on phase composition in the composites obtained after the process of sintering.

Thesis: Increase in the amount of addition of ZrO_2 zirconium phase, modified with 8% wt. and 20% wt. Y_2O_3, to hydroxyapatite bioceramics leads to reduction of shrinkage triggered by sintering of the mixture prepared from both powders. Zirconium phase in HA + ZrO_2 mixture stabilizes the dimensions of final, sintered composite.

[6] Being a source of substances that induct bone genesis in the tissues surrounding the bone defect
[7] The process of bone creation on connective-tissue or cartilaginous base

In order to prepare sinters based on HAp, powder metallurgy method was employed in this study, which allowed to obtain porous materials with beneficial biofunctional properties.

The obtained materials, as a group of biomaterials which are widely used in bone surgeries, were then subjected to structural and phase tests. The *mathematical description that allows for assessment of volume shrinkage in HAp + ZrO_2 sinters* was developed after the process of sintering, which is a significant result of this work.

3.1 Procedure for the experiment

During the investigations the following powders were used:

- HAp ($Ca_{10}(PO_4)_6(OH)_2$) with average particle size of 50 micrometers, characterized by high purity level (over 99%wt.): Pb = 0.8ppm, As<1.0 ppm, Cd, Hg<0.1 ppm; Ca/P = 1.67,
- ZrO_2 oxide with addition of 8% (wt.) Y_2O_3 (YSZ – Yttria Stabilized Zirconia) (Fig. 6),
- ZrO_2 oxide with addition of 20% wt. Y_2O_3.

Both zirconium oxide powders were 100%crystalline, while their grains were of regular, spherical shape of grains.

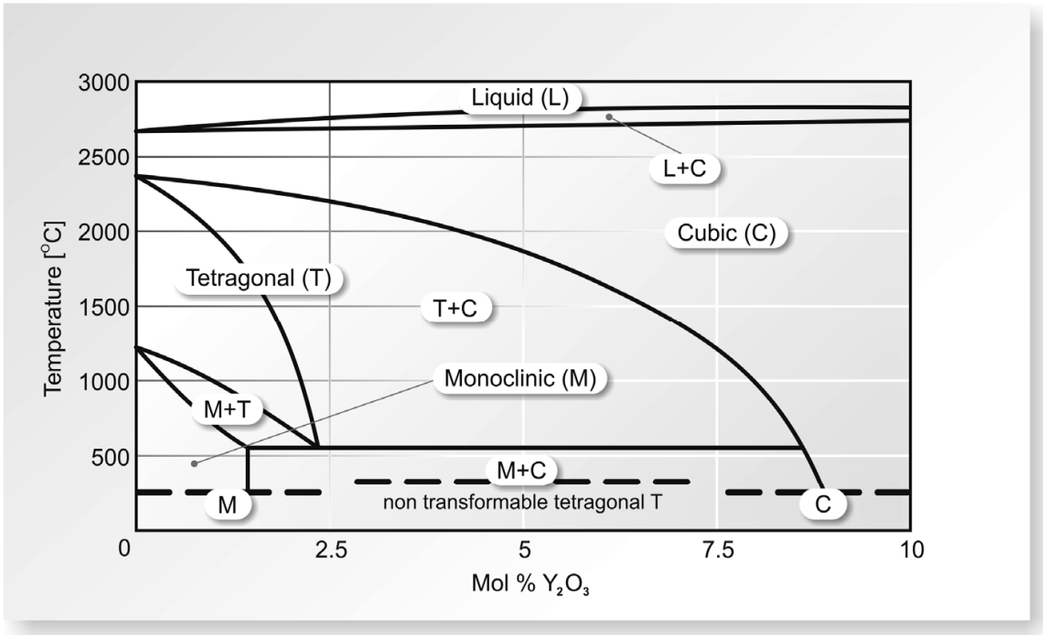

Fig. 6. Types of zirconium ceramics depending on the content of Y_2O_3 modifying phase

The composites based on hydroxyapatite with addition of different content of the both zirconium ceramic powders modified with ytrrium oxide were prepared:

- 100% HAp,
- (90%÷30%) HAp + (10%÷70%) YSZ; where: (YSZ-Ytrria Stabilized Zirconium, means ZrO_2+8%wt.Y_2O_3)
- (80%÷30%) HAp + (20%÷70%) ZrO_2 + 20%wt. Y_2O_3

3.2 Stereological tests of the used powders

Histograms of distribution of stereological parameters in the investigated powders, whose morphology is shown in Fig. 7, are presented in Fig. 10-12 (for hydroxyapatite) and in Fig. 8, 13-15 (for zirconium ceramics with addition of 8%wt. Y_2O_3) and Fig. 9, 16-18 (for zirconium ceramics with addition of 20%wt. Y_2O_3).

Shape factor R was calculated using the following formula:

$$R=L^2/(4\pi A) \quad (1)$$

where: L-particle circumference, A-particle surface area.

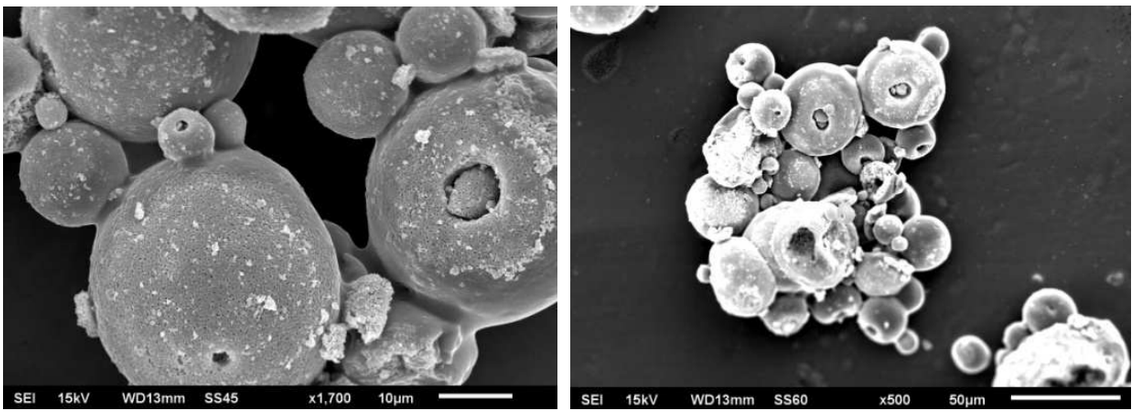

Fig. 7. Microphotograph of the powder: HAp

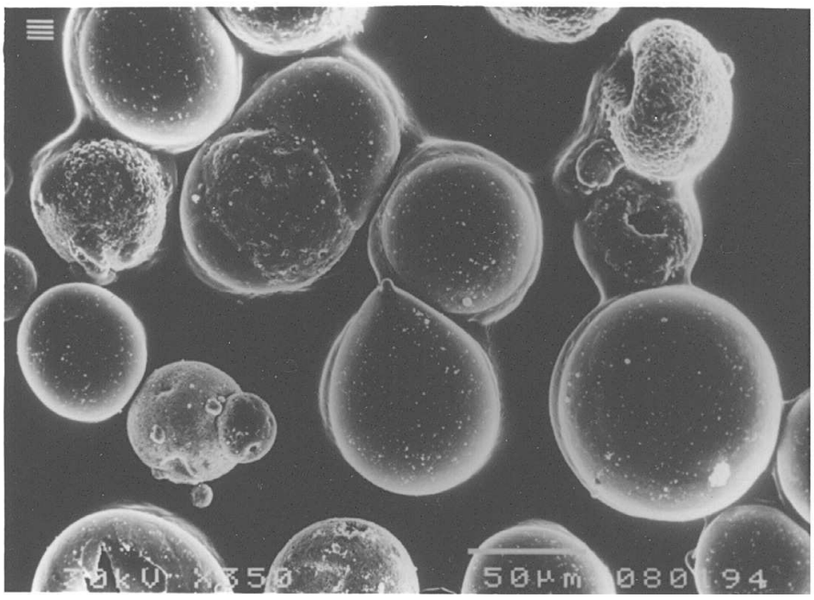

Fig. 8. Microphotograph of the powder: YSZ

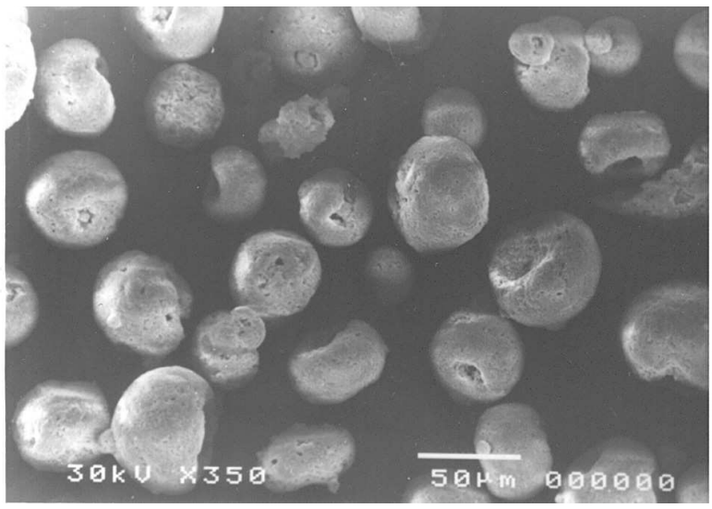

Fig. 9. Microphotograph of the powder: ZrO_2+20%Y_2O_3

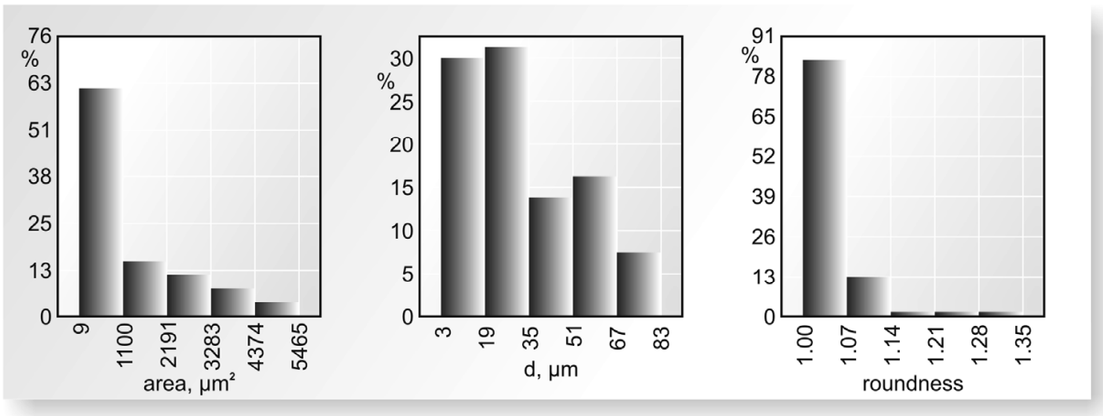

Fig. 10. Surface area histogram in particle of HAp powder

Fig. 11. Chord histogram in particles of HAp powder

Fig. 12. Shape factor histogram in particles of HAp powder

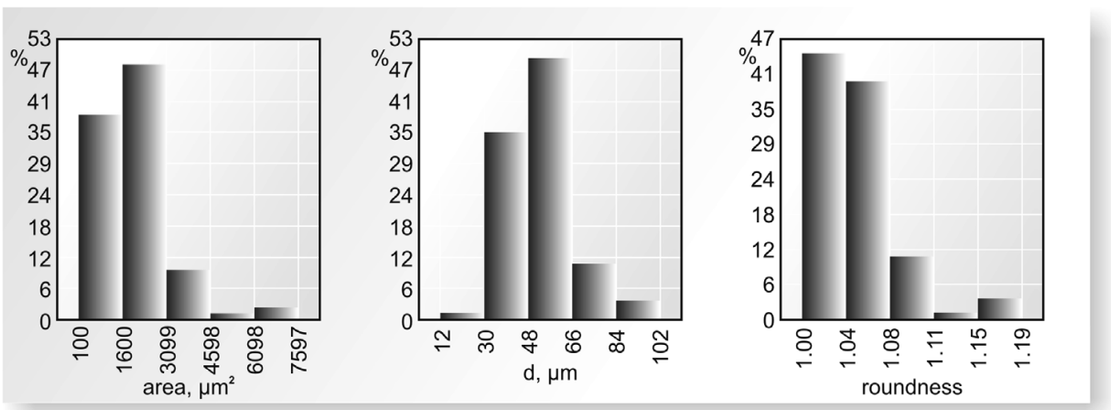

Fig. 13. Surface area histogram in particle of ZrO_2 + 8wt.% Y_2O_3 powder

Fig. 14. Chord histogram in particles of ZrO_2 + 8wt.% Y_2O_3 powder

Fig. 15. Shape factor histogram in particles of ZrO_2 + 8wt.% Y_2O_3 powder

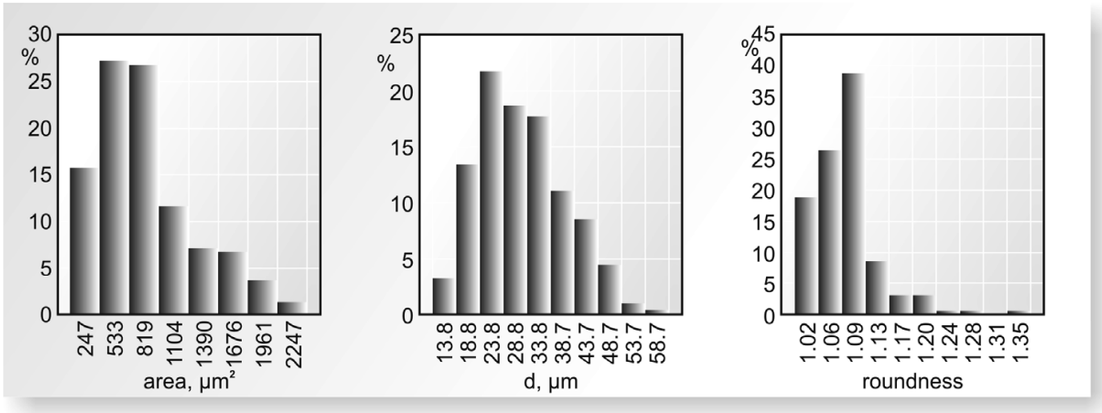

Fig. 16. Surface area histogram in particle of ZrO_2 + 20wt.% Y_2O_3 powder

Fig. 17. Chord histogram in particles of ZrO_2 + 20wt.% Y_2O_3 powder

Fig. 18. Shape factor histogram in particles of ZrO_2 + 20wt.% Y_2O_3 powder

After homogenization of the mixtures of selected particular compositions, powders were then axially compressed with the load of 110 MPa (Fig. 19) and dried in laboratory dryer. As a result of the procedure the moulded pieces were obtained with nominal dimensions of: ϕ=30mm, h=5mm.

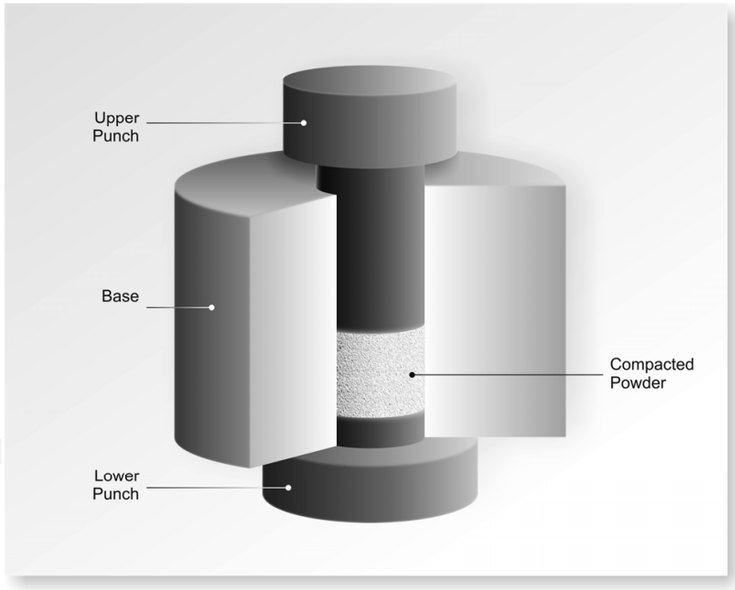

Fig. 19. Diagram of the mould used for powder compaction

Compaction of the powders was carried out in the following stages:

- movement of particles in relation to each other,
- elastic deformations in particles,
- crushing of particles.

The obtained moulded pieces where then subjected to the process of sintering at the temperature of 1100-1300^{0}C for two hours.

As a result of physical and chemical processes that accompany the process of sintering, a change in properties and dimensions of the moulded pieces occurred.

3.3 Microstructure tests

Macroscopic changes in the product during sintering are a result of numerous physical and chemical processes that occur in the material. The moulded pieces were subjected to microstructure tests using JEOL JSM 5400 scanning microscope.

Analysis of one-phase system (100 % HA) (Fig.20) and sinters of HA+ZrO_2 before and after sintering (1100-1300^{o}C) (Fig.21) reveals that grains after the process of sintering were partially crushed and they were adjacent to each other. After the process of sintering a reduction in porosity (i.e. in number and size of pores) occurred.

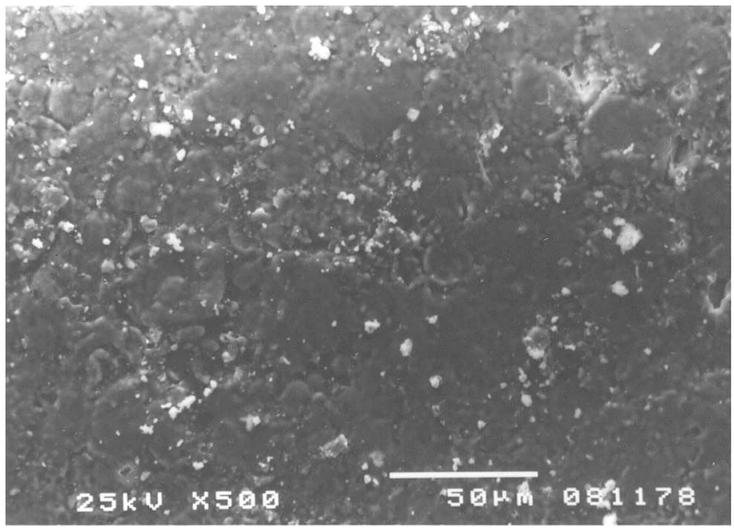

Fig. 20. 100% HAp powder after sintering

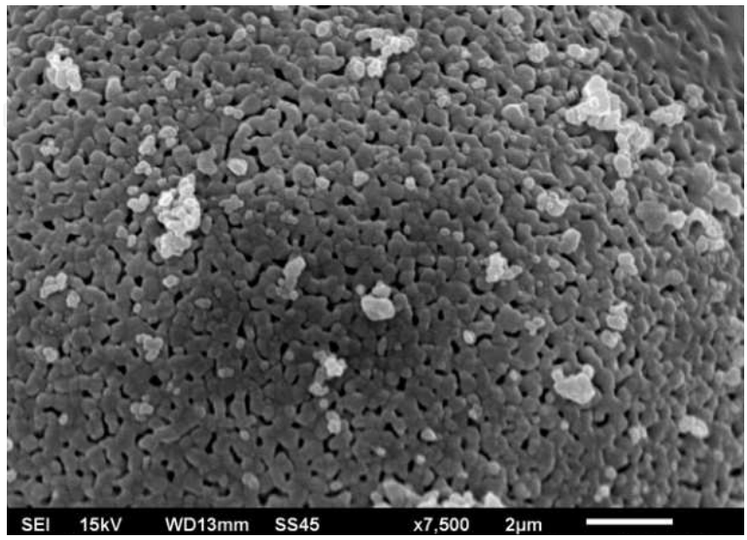

Fig. 21. Powder of: 50%HA + 50% ZrO_2 (8%wt.Y_2O_3) after sintering

Analysis of Hap+ZrO_2 sinters reveals that decreases largeness of grain and increase largeness of pore.

In the case of calcium orthophosphates, several specific processes occur during sintering. Firstly, moisture, carbonates and all other volatile chemicals remaining from the synthesis stage, such as ammonia, nitrates and any organic compounds, are removed as gaseous products. Secondly, unless powders are sintered, the removal of these gases facilitates production of denser ceramics with subsequent shrinkage of the samples. Thirdly, all chemical changes are accompanied by a concurrent increase in crystal size and a decrease in the specific surface area. Fourthly, a chemical decomposition of all acidic orthophosphates and their transformation into other phosphates takes place.

3.4 X-Ray structural analysis

It seems to be necessary, from the standpoint of wider use of composite materials, to determine phase stability in the obtained composites. After the sintering process, phase analysis was carried out using Seifert 3003 T-T X-ray diffractometer with radiation of wavelength of $\lambda_{K\alpha Co}$=0,17902 nm.

First stage encompassed phase analysis of the powders. X-ray quality analysis of hydroxyapatite powder revealed its 100% crystallinity and presence of hexagonal phase of HA with the following parameters of the cell: a = b = 9,418 nm, c= 6,884 nm, space group P63/m.

As results from the analysis of the obtained diffractogram, ZrO_2 modified with 8% wt. of Y_2O contains two polymorphous modifications of zirconium dioxide: tetragonal phase and small amount of monoclinic phase.

ZrO_2 powder with addition of 20% wt. of Y_2O_3 mainly consisted of monoclinic and small amount of regular phase. Lack of tetragonal phase, which indicates stabilization of zirconium phase proves undoubtedly that the powder is only a mixture of the two oxides rather than their solution.

Analysis of phase composition for sintered samples of 100% HA revealed that they are composed of hexagonal phase – HAp and TCP_{α}, CaO phases.

Diffractogram of sinters with analysed percentage contents of both powders are presented in: Fig. 22 for HA+ ZrO_2 (modified with 8wt.% Y_2O_3) and Fig. 23 for HA + ZrO_2 sinters (with addition of 20wt.% Y_2O_3).

Analysis of diffractograms of sinters that contain from 20-60% of YSZ phase revealed presence of HA phase, ZrO_2 with tetragonal modification, insignificant amount of TCP_{α} and CaO phase. The amount of TCP_{α} and CaO decreases as zirconium phase addition rises for all sintering temperatures.

The results of analysis of sinter diffractograms with addition of ZrO_2+20%Y_2O_3 phase were comparable – as HA, TCP_{α} and insignificant amount of CaO phase (that gradually disappears as zirconium phase addition rises) occur in it. The peaks from tetragonal ZrO_2 phase were also observed; its presence seems to be of much interest since monoclinic phase predominated in initial powder.

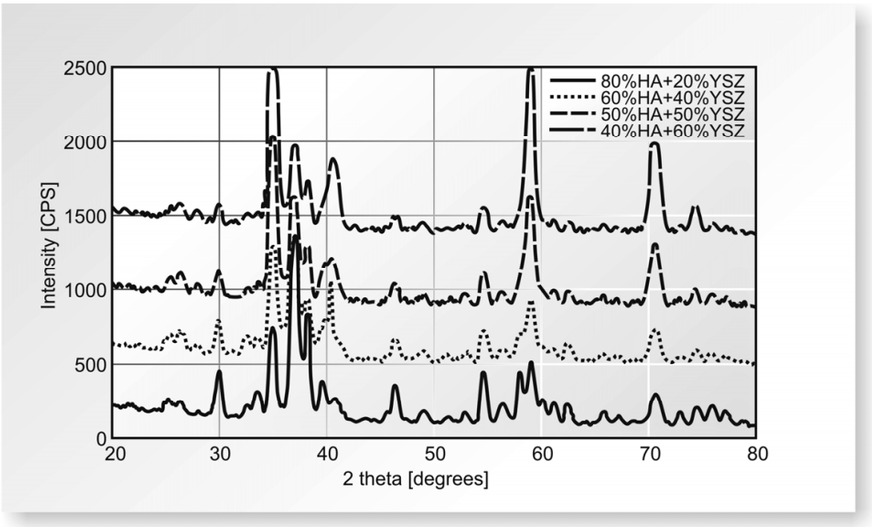

Fig. 22. Collective diffractogram for sinters of HA+ZrO_2 modified with 8% wt. Y_2O_3

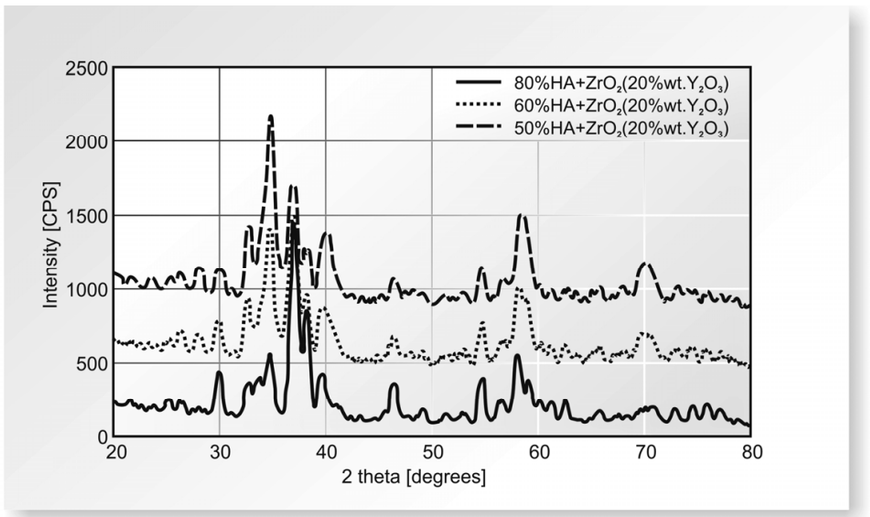

Fig. 23. Collective diffractogram for sinters of HA + ZrO_2 with addition of 20% wt. Y_2O_3

The process of sintering of HA + ZrO_2 (+20%Y_2O_3) mixtures caused, according to the investigations, decline in monoclinic modification and its transition into tetragonal modification. Thus, the applied treatment resulted in m↔t transition, i.e. transformation of monoclinic form into tetragonal one took place. This fact can be explained by impact of CaO phase that appeared during hydroxyapatite decomposition on stability of tetragonal phase. Moreover, presence of monoclinic modification of ZrO_2 in ZrO_2+20%wt.Y_2O_3 powder proves undoubtedly the absence, in the case of the analysed composition, of solid solution of Y^{+3} ions in crystallographic network of zirconium oxide. The process of sintering could have led to appearance of such solutions and also to stabilization of tetragonal phase.

The conducted analysis allows to observe that addition of zirconium phase impacts on rise in temperature of hydroxyapatite decomposition, which manifests in decline in CaO and

TCP_α phase and rising addition of ZrO_2+8wt.%Y_2O_3 and ZrO_2+20%wt.Y_2O_3 phases in powder mixtures.

3.5 Apparent density of moulded pieces and sinters

During development of materials for implants one must consider proper density of HA+ZrO_2 composites. Proper level of density must ensure that specific strength properties are obtained as well as necessary open porosity that allows for ingrowing of the implant. In order to achieve this, apparent density measurements in the obtained moulded pieces and sinters were carried out. The results are presented in Fig. 24 and 25.

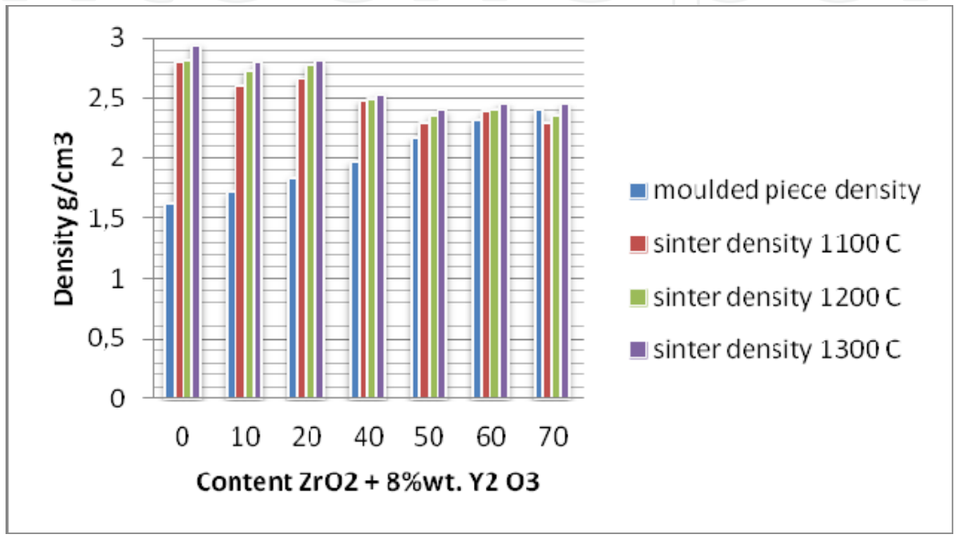

Fig. 24. Change in sample density depending on percentage content of ZrO_2 + 8 % wt. Y_2O_3 before and after sintering

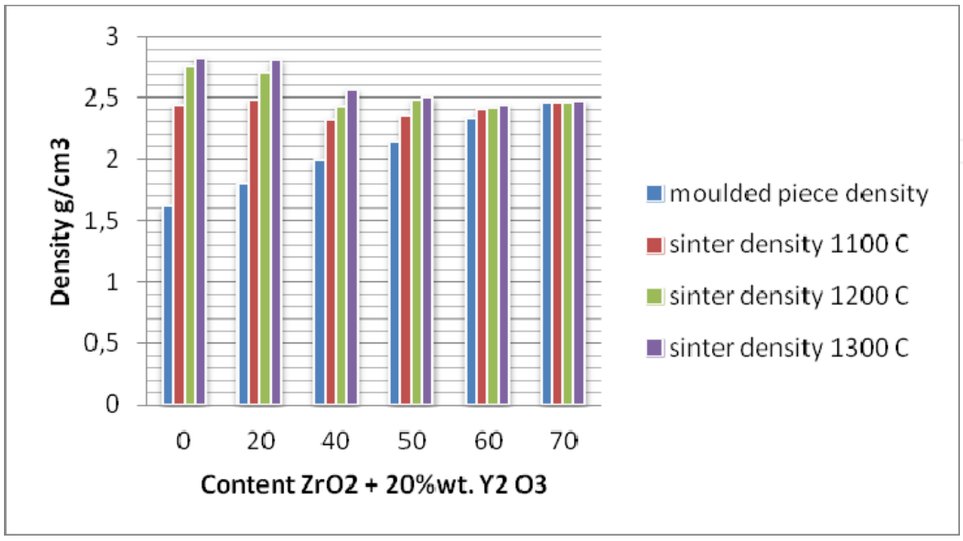

Fig. 25. Change in sample density depending on percentage content of ZrO_2 + 20% wt. Y_2O_3 before and after sintering

Densities of moulded pieces and sinters assessed in the case of addition of the same amounts of ZrO_2 modified with 8% wt. as well as 20% wt.Y_2O_3 to HA were comparable. Density of moulded pieces (HA+ ZrO_2) increases with addition of zirconium oxide, which is connected with difference in the value of density in both powders (ρ_{HA}=3gcm^{-3}, ρ_{ZrO2}=6gcm^{-3}). In consideration of the density in each sample before and after sintering, it is remarkable that the difference between density of a moulded piece and the sinter decreases with addition of zirconium phase. A density of sintered pieces increases with sintering temperatures.

This fact proves that addition of zirconium ceramics (regardless of ittria content used as modifier) stabilizes dimensions of the sintered composite based on HA.

Analysis of test results reveals that, in the case of composite samples with addition of ZrO_2 modified with both 8% wt. and 20% wt.Y_2O_3, density of the moulded piece equals density of the sinter at the content of ca. 70% of zirconium phase. This means that the obtained sinter is characterized by zero shrinkage after the treatment.

3.6 Mathematical description of the shrinkage in HA+ZrO_2 composites

An essential issue is to determine exact percentage content of addition of ZrO_2 phase to the mixture in terms of their impact on dimensional stability.

In order to formulate generalized dependencies in the obtained sinters, the analysis of dependencies between content of zirconium phase and the shrinkage was carried out using correlation and regression of two variables.

For the obtained experimental points linear regression equations were matched by means of least squares method, correlation coefficient was calculated and the tests were made with the significance level of α=0.05 using the following dependencies:

- significance test for correlation coefficient

$$t = \frac{r}{\sqrt{1-r^2}}\sqrt{n-2} \tag{2}$$

where: n – number of degrees of freedom, r – correlation coefficient

- significance test for coefficients of regression equation

$$t = \frac{A-A_0}{S_r}\sqrt{\sum_{i=1}^{n}\left(x_i-\bar{x}\right)^2}\ ;\ S_r = \sqrt{\frac{1}{n-2}\sum_{i=1}^{n}\left(y_i-\hat{y}\right)^2}\ ;\ t = \frac{B-B_0}{S_r}\sqrt{\frac{n\sum_{i=1}^{n}\left(x_i-\bar{x}\right)^2}{\sum_{i=1}^{n}x_i^{\,2}}} \tag{3}$$

where: S_r - remaining deviation, A, A_0 – values of direction component, B, B_0 – absolute term.

- confidence interval for direction component of simple regression

$$P\left[A - t_\alpha \frac{S_r}{\sqrt{\sum_{i=1}^{n}\left(x_i-\bar{x}\right)^2}} < A' < A + t_\alpha \frac{S_r}{\sqrt{\sum_{i=1}^{n}\left(x_i-\bar{x}\right)^2}}\right] = 1-\alpha \tag{4}$$

where: value of T-Student statistics for n-2 degrees of freedom and the accepted confidence level 1-α.

- asymptotes equation for confidence corridor

$$\hat{y}_1 = B_1 + A_1 \;\; \hat{y}_2 = B_2 + A_2 x \tag{5}$$

- confidence corridor for simple regression

$$P\left[\hat{y} - t_\alpha S_{\hat{y}_i} < \tilde{y} < \hat{y} + t_\alpha S_{\hat{y}_i}\right] = 1 - \alpha \quad S_{\hat{y}_i} = S_r \sqrt{\frac{1}{n} + \frac{(x_i - \bar{x})^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}} \tag{6}$$

The results of the performed calculations are presented in Fig. 26-27. These calculations show strong dependence between the contents of zirconium phase and sample shrinkage after sintering process. It was also proved by high values of correlation coefficient $r^2>0.98$.

On the basis of regression curves one can determine the content of zirconium phase at which sinters based on hydroxyapatite show zero shrinkage. In the case of HAp + ZrO_2 (8%wt. Y_2O_3) ceramics, a simple extrapolation method enabled determination of ZrO_2+8%wt. Y_2O_3 powder content which ensured zero shrinkage at the level of 70.6% wt. Content interval determined from confidence corridor amounts to from 65% to 76% wt.

Similar considerations were made for HAp + ZrO_2 (20 %wt. Y_2O_3) ceramics and they enabled determination of the amount of addition ZrO_2+20 %wt. Y_2O_3 powder that corresponded with zero shrinkage in sinter at the level of 76% wt.. Confidence corridor range for these samples ranged from 70% to 82% wt.

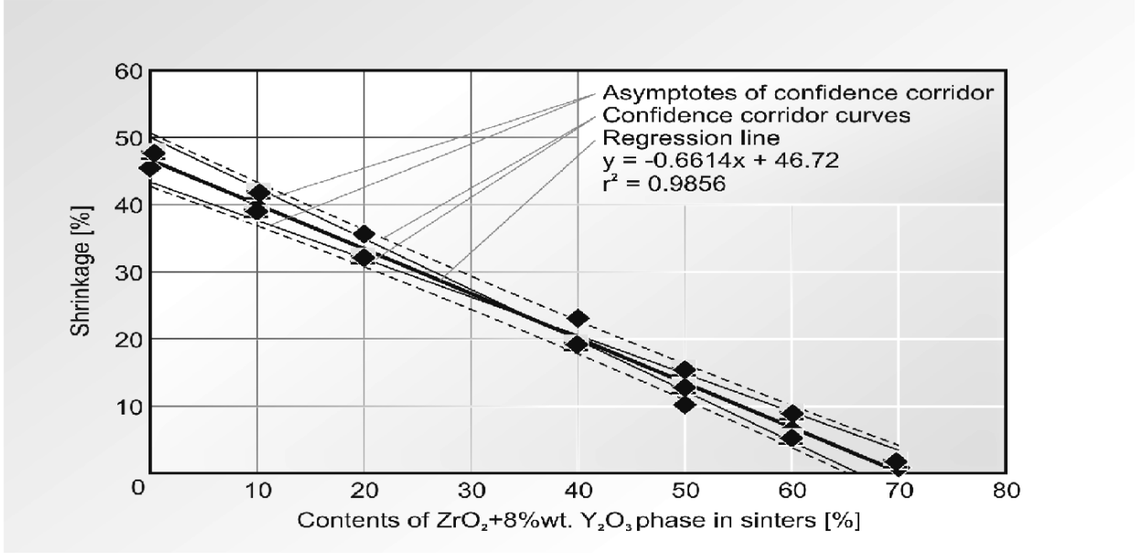

Fig. 26. Correlation chart with confidence corridor for HAp + ZrO_2 (8 %wt. Y_2O_3) sinters in 1100-1300°C

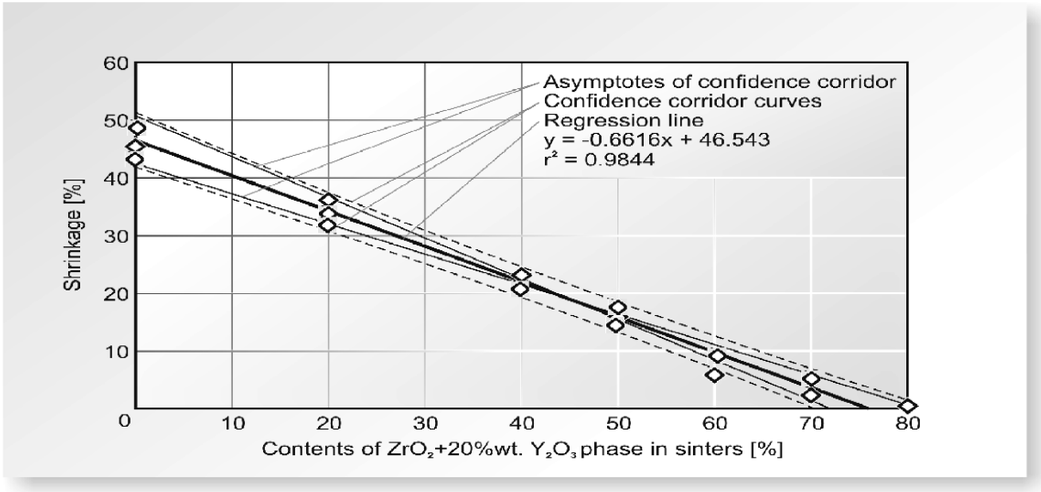

Fig. 27. Correlation chart with confidence corridor for HAp + ZrO_2 (20 %wt. Y_2O_3) sinters

4. Summary and conclusions

- A sintering procedure appears to be of a great importance to manufacture bulk bioceramics with the required mechanical properties.
- Hydroxyapatite ceramics have been found to be one of the best implantation materials successfully used in bone surgeries and dentistry. This ceramics allows for their easy connection with other types of materials, which creates opportunity for development of composites for medical applications.
- For the purposes of this work and creation of ceramic composites (HA+ZrO_2), powder metallurgy method was employed, which allowed to receive porous materials based on hydroxyapatite.
- Phase analysis of the sinters obtained from mixtures of powders (based on hydroxyapatite with addition of zirconium oxide modified with 8% wt. Y_2O_3 and 20% wt. Y_2O_3 revealed presence of HA phase as well as TCP_α and CaO phases that prove decomposition of hydroxyapatite. The investigations also revealed that addition of zirconium phase impacts on rise in temperature of hydroxyapatite decomposition, which manifests in decline of CaO and TCP_α phases with addition of ZrO_2+8wt.%Y_2O_3 ZrO_2+20%wt.Y_2O_3 phases in powder mixtures.
- In consideration of the density in each sample before and after sintering, it is remarkable that the difference between density of a moulded piece and the sinter decreases with addition of zirconium phase. This fact proves that addition of zirconium ceramics (regardless of ittria content used as modifier) stabilizes dimensions of the sintered composite based on HA.
- From the standpoint of common use of hydroxyapatite and HAp-based composites (with addition of ZrO_2 phase) for medicine, it is of key importance to determine such percentage content of ZrO_2 phase addition in the mixture that invariable or predictable dimensions of the implant or coating are maintained after the process of sintering. The presented mathematical description enables assessment of the amount of zirconium oxide (with different addition of stabilizing Y_2O_3 phase) in the mixture of powders that ensures zero shrinkage in sinters.

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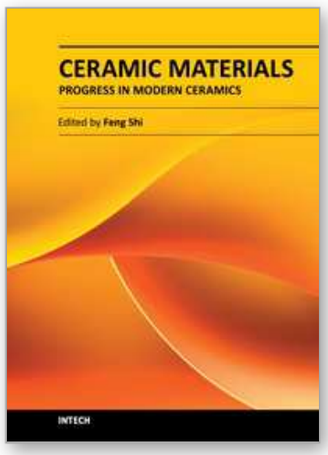

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