INVESTIGATION ON THE MICROSTRUCTURE OF THE HAP AND YSZ COMPOSITES

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Abstract: Group of bioceramic materials includes, among others, hydroxyapatites (HAp, OHAp, HA), which, due to their specific properties are widely applied. These compounds are currently present in bone systems of human and animal bodies. One of the solutions for improvement of poor properties of HAp is addition of zirconium oxide which is characterized by high biological tolerance and enhanced mechanical properties.
Application of bioceramic materials as coatings for implants introduced into human body due to their bioinertness and biocompatibility enables overcoming immunology barriers. One of the fundamental advantages of ceramic materials is their positive impact on human tissues.
The investigations involved creation of composites through single-axial compaction of two ceramic powders (HAp+YSZ) and then their sintering at the temperature of 1300°C for two hours.
The aim of the investigations was to determine thermal stability of hydroxyapatite (Fig. 1) and HAp + YSZ (Partially Stabilized Zirconia) (Fig. 2) and impact of addition of YSZ (8%wt. Y_2O_3 stabilizing ZrO_2) on phase composition of the prepared composites after the process of sintering.
Investigations of the structure have been performed using JEOL JSM 5400 (Fig. 4, 5) scanning microscope while phase composition have been carried out by means of Seifert 3003 T-T X-ray diffractometer (Fig. 6, 7).

1. INTRODUCTION

Recent years have seen considerable improvement in development of special-purpose properties used in medicine. In particular, this encompasses group of materials used for implants.

Application of bioceramic materials as coatings for implants introduced into human body due to their bioinertness and biocompatibility enables overcoming immunology barriers. One of the fundamental advantages of ceramic materials is their positive impact on human tissues.

European Society for Biomaterials clearly defines biomaterials as a group of natural or synthetic substances which can replace or overcome functions of parts or a whole tissue or organs (Hartmann and Jager, 2001).

A group of minerals such as hydroxyapatites (HAp, OHAp, HA), due to their specific properties covers wide application range in biotechnology. They are the compounds which, from chemical and mineralogy point of view, are similar to inorganic substances which form human bone tissue or teeth.

Considerations of human bone system issues is by all measures justified due to progressing demand for a variety of implants.

Literature studies enable statement that a threshold of opportunities of improvements in biotolerance and properties of applied bioceramic implants has already been reached. Currently the most promising materials for prosthetics are composites (Khalil et al., 2007; Chevalier et al., 2005; Inzuka et al., 2005; Sung and Kim, 2003; Cheng et al., 2005; Rapacz-Kmita et al., 2005; Yoshida et al., 2006; Chiu et al., 2007; Kalkura, 2003; Heimann, 2006.

2. MATERIALS AND INVESTIGATIONS METHODOLOGY

Hydroxyapatite powder of $Ca_{10}(PO_4)_6(OH)_2$ (Sulzer-Metco) (with 99% purity and the ratio of Ca/P = 1.67) and ZrO_2 zirconium oxide powder modified with 8%wt. Y_2O_3 (YSZ) were used for investigations.

Morphology for the applied powders are presented in Fig. 1, 2.

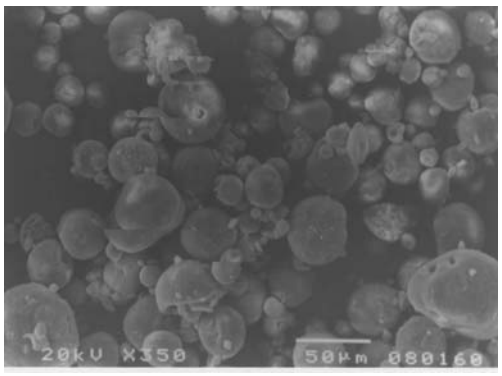

Fig. 1. Morphology of hydroxyapatite powder, magn. 350x

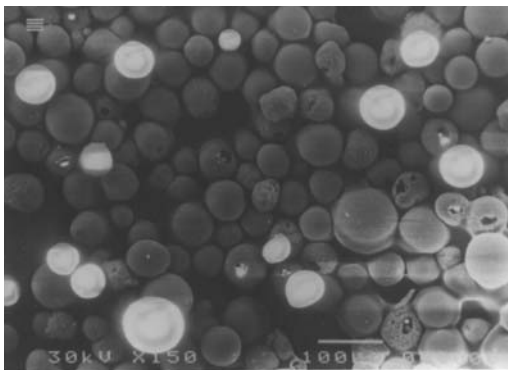

Fig. 2. Morphology of YSZ powder, magn. 350x

In order to prepare composites the following granulation values for the powders were used: HAp – ca 50 μm, ZrO_2 – 80 μm. Both powders have regular, spheroid shape of grains.

Powders were then subject to grinding in ball grinder in order to obtain even mixing of both powders.

The purpose of the investigation was to obtain bioceramic composites with the following rates by weight: 100 % HAp , HAp + 10% wt. YSZ, HAp + 30% wt. YSZ. These powders were formed through their single-axis compaction inside a die with load of 70 MPa (Fig. 3).

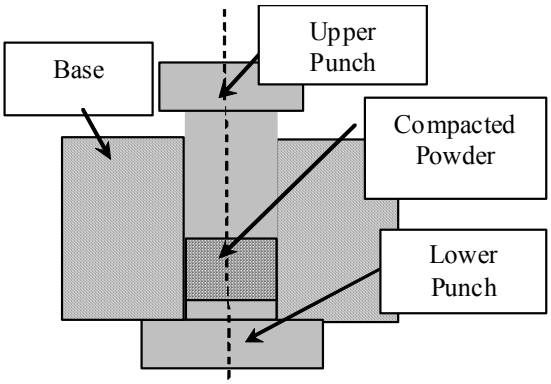

Fig. 3. Diagram of the die used for powder compaction

A result of compaction was a form, commonly referred to as 'moulded piece'. Compaction of the powders was carried out in the following stages:

- dislocation of particles in relation to each other,
- plastic strain of particles,
- crushing of particles.

The particles moving in relation to each other as a result of the compaction pressure had to overcome friction forces and than the breaking of 'bridges' which had appeared during powder loading occurred.

Next stage of bioceramic composite preparation was sintering of the prepared moulded pieces. This process consisted in soaking of the compacted powder at the temperature lower than melting point of the applied components in order to compact it into a solid piece. Sintering temperature was determined as 1300 ^oC for 2 hours.

As a result of physical and chemical processes which accompany the process of sintering a change in properties and dimensions of moulded pieces was observed.

During investigations some microscopic tests of moulded pieces before and after the sintering process in order to analyse one phase system were carried out. Microstructure of moulded piece before sintering is presented in Fig. 4, while after sintering – Fig. 5.

Analysis of one phase system (100 % HAp) before and after sintering reveals that the grains after the process of densification were partially crashed and they adhered to each other. After the process of sintering a visible reduction in porosity occurred.

In order to analyse phase stability of the produced composites (which is necessary in the aspect of their prospective application) after sintering, a phase analysis was carried out using Seifert 3003 T-T X-ray diffractometer using radiation with wavelength of $\lambda_{K\alpha Co}$=0.17902 nm. The results of investigations for all created composites are presented in Fig. 6 and 7.

Hydroxyapatite begins changing its phase composition over the temperature of 900 ^oC due to loss of water and appearance of partially or totally dehydrated oxyhydroxyapatite.

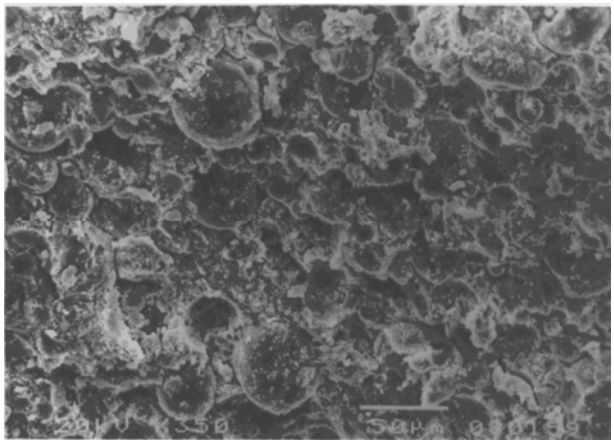

Fig. 4. Microstructure of the compacted powder with 100 % HAp

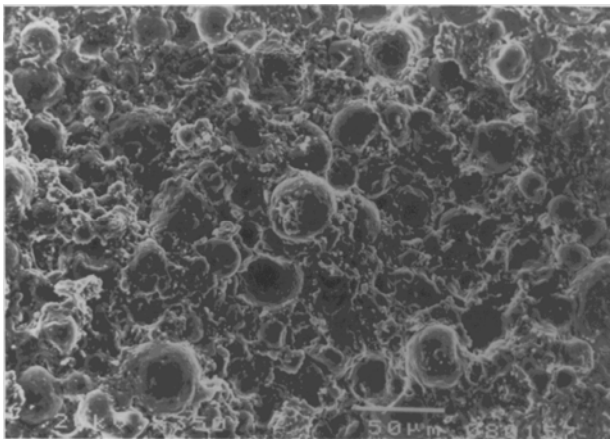

Fig. 5. Microstructure of the compacted and sintered powders with 100 % HAp

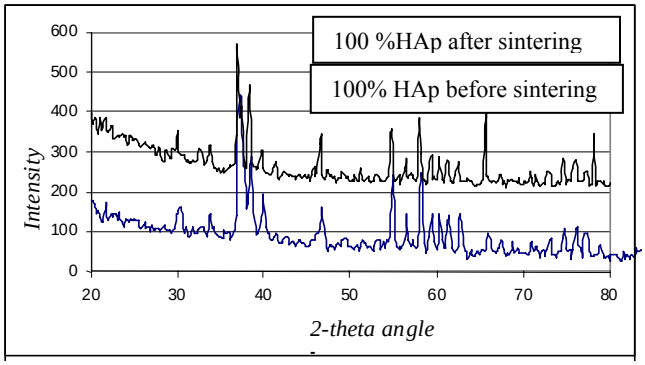

Fig. 6. Diffractogram of 100% HAp moulded piece before and after sintering at the temperature 1300^0C for 2 hours

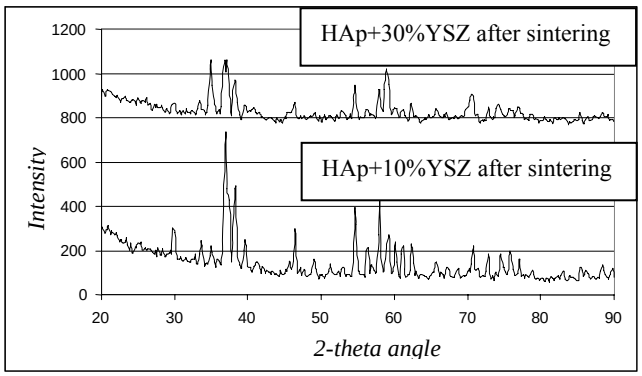

Fig. 7. Diffractogram of moulded piece HAp +10 %wt. PSZ and HAp + 30 %wt. PSZ sintered at the temperature of 1300^0C for 2 hours

Phase analysis of the samples made of 100% hydroxyapatite, both before and after the process of sintering, have not revealed any phase changes (Fig. 6). HAp phase (hydroxyapatite) with $Ca_{10}(PO_4)_6(OH)_2$ formula occurred throughout the volume; it crystallises in hexagonal system with the following unit cell parameters: a=b=9.418 nm, c= 6.884 nm and space group of P63/m.

Diffractograms obtained for HAp +10 %wt. and HAp +30 %wt. composites revealed presence of two phases: HAp and ZrO_2 with tetragonal cell (Fig. 7). Moreover, X-ray tests excludes the fact of the presence of β-TCP phase, described by Yun-Mo Sung and Dae-Hee Kim's team in Sung and Kim (2005); the authors argued that its contents increased as a result of rise in YSZ percentage value.

3. CONCLUSIONS

Subject of investigations was composites made of HAp powder and HAp +YSZ powders with granulation of 50 μm and 80μm, respectively. Composites were created by single-axis compaction in die and then sintering at the temperature of 1300 ^{o}C during two hours.

Macro- and microscopic observations of samples before and after sintering revealed contraction in volume as a result of reduction in porosity, maintaining primary shape of samples.

On the basis of X-ray analysis no phase decomposition in hydroxyapatite or in HAp – based composites with addition of YSZ (ZrO_2 – zirconium oxide stabilized with 8%wt. yttrium oxide Y_2O_3) after the process of sintering at the temperature of 1300 ^{o}C has been revealed.

The applied sintering temperature and addition of ZrO_2 have not caused appearance of unfavourable, from the chemical stability point of view, β-TCP phase.

Analysis of X-ray and structural tests proved thermal stability of the applied hydroxyapatite powder.

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