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Hydroxyapatite/zirconium oxide ceramics obtained by spark-plasma sintering

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Powdered samples of hydroxyapatite and oxoapatite were obtained via sol-gel and hydrothermal method, respectively. Powder X-ray diffraction analysis showed absence of substances that could adversely affect the biocompatibility of the compounds obtained. Ceramic samples with zirconium oxide were obtained from apatites by spark plasma sintering and their physicochemical and mechanical attestation were carried out.

Keywords: *hydroxyapatite, zirconium oxide, ceramics, spark-plasma sintering*

1. Introduction

One of the most important branches of modern materials science is the development of new materials for manufacturing bioimplants - artificial products for partial or complete replacement of human solid tissues [1].

The main efforts in developing such materials are aimed to attain necessary biological properties that ensure the survival of human cells on the surface of an implant as well as to gain multiple mechanical properties [2,3].

The most biologically compatible materials are those based on compounds with apatite structure, in particular, hydroxyapatite (HAp) $Ca_{10}(PO_4)_6(OH)_2$. This substance is a structural and chemical analogue of bone tissue, so that not only does it resist corrosion and encapsulation, but also stimulates the processes of osteogenesis in a living body. Apart from hydroxyapatite, other mainly bioinert calcium phosphates like - β-tricalcium phosphate $Ca_3(PO_4)_2$, oxoapatite (OAp) $Ca_{10}(PO_4)_6O$, calcium biphosphate $Ca_2P_2O_7$, which are mainly bioinertic, are also used [4-5]. Unfortunately, the mechanical properties of materials based on those substances do not meet requirements for a successful replacement of bone tissue.

One of ways to improve the mechanical properties of materials based on calcium phosphates is their joint use with other, usually inorganic, bioinert substances. Basically, we are talking about oxides of titanium and zirconium.

Zirconium oxide is also widely employed as a biocompatible material for the creation of osteo-replacing implants. However, earlier attempts to obtain implants from ZrO_2 alone are anything, but successful. Despite the high mechanical performance, the materials were found bioinert [6-9].

With that being said, the goal of the work is to obtain ceramics based on zirconium oxide and biocompatible compounds of apatite structure, as well as to determine their mechanical properties.

2. Experiment

Samples of apatite powders were acquired by two methods. Sol-gel technique allows one to obtain particles of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, using mild conditions: low temperatures and atmospheric pressure. The initial reagents (calcium nitrate, phosphoric acid) were mixed in keeping with required ratio to maintain the proportion characteristic of stoichiometric hydroxyapatite (n(Ca)/n(P) = 5/3), to sustain the optimum pH = 7 a 1 M sodium hydroxide solution was added. The mixture was kept at 37°C for an hour, then centrifuged, washed with distilled water and air-dried [10].

To obtain the oxoapatite $Ca_{10}(PO_4)_6O$, the hydrothermal method was opted for. In this case, the solution of the initial reagents (calcium nitrate, ammonium hydrogen phosphate, ammonium hydroxide) was kept for 8 hours in a sealed reactor at a temperature of 120°C. Using this approach mimics conditions maintained in a geological environment typical which are conducive for the formation of minerals of apatite structure due to the increased pressure caused by overheating of water above the boiling point.

PXRD was performed on a Shimadzu XRD-7000 X-ray diffractometer using the DIFFRAC plus Evaluation package (Release 2009) and PDF-2 (Release 2009) database.

The technology of spark plasma sintering (EIPS or SPS) was used for production of ceramics. "Dr. Sinter model SPS-625 " was used since it affords real-time shrinkage kinetics analysis of powders with various temperature increment supplied by high-speed heating in a real time by means of using precision dilatometer. On top of that, the following parameters like heating rate, applied pressure can be varied directly during the sintering process, so as to perform stepwise sintering regimes, etc.

Manufacture of ceramic samples was implemented as follows. A homogeneous mixture of powders was sintered at the rate of to 600°C with the increment being 100 deg/min, to 1150°C with 50 deg/min respectively. The sintering pressure was 70 MPa. Cooling was uncontrolled.

The density of the ceramics was determined by hydrostatic weighing with analytical balance Sartorius CPA 225D.

Certification of hardness and fracture toughness of the samples were carried out by usage of an automated micro-hardness meter "Struers Duramin-2" for measurement of the diagonal distances of a diamond pyramid (indentor) imprint on the polished surface of the sample. Dimensions of the diagonals of the indenter equal 500 μm, the angle at the top of the pyramid equals 136 ° (Figure 1). The identification of the Vickers diamond pyramid was carried out at the load P = 2000 g, the loading time was t = 30 s.

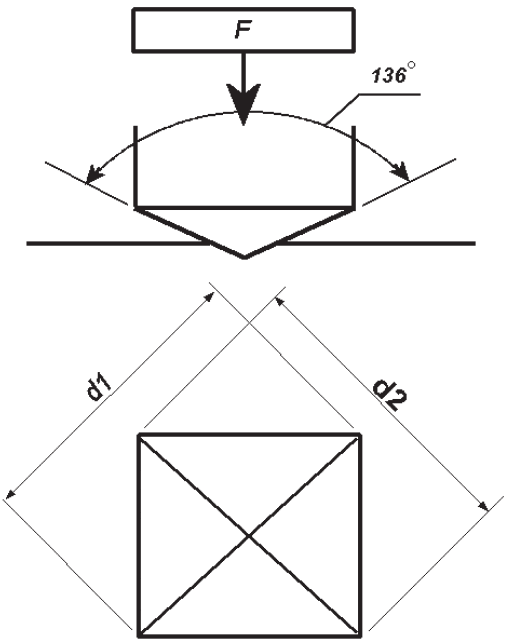

Figure 1. Scheme of indenter indentation into the sample.

Coefficient of crack resistance (K_{IC}) was determined on the basis of the length of radial cracks from the indentor Vickers indentation. The K_{IC} values (MPa · $m^{1/2}$) were calculated using the Palmqvist method:

$$K_{IC} = 0.016 \frac{P}{c^{3/2}} \sqrt{E/H_v},$$

where P is the load on the indenter, g; c is the average distance from the center of the print to the end of the crack, m; - Vickers hardness, GPa; E is the modulus of elasticity of the material, GPa.

The microstructure of the resulting ceramic samples was examined using a scanning electron JEOL JSM-6490 with a tungsten cathode.

3. Results and discussion

PXRD data of the obtained hydroxyapatite powders evinces formation of hydroxyapatite Ca10(PO4)6(OH)2 (HAP) of hexagonal modification as result of Sol-gel technique employed (Fig. 2-top) [11]. In case of the hydrothermal synthesis method, oxoapatite (OAP) of the composition Ca10(PO4)6O with 10% impurity of calcium biphosphate Ca2P2O7 was obtained (Fig. 2-middle) [12,13]. Zirconium oxide is an equimolar mixture of two polymorphic modifications: monoclinic, baddeleyite-corresponding to the mineral, and metastable tetragonal (Fig. 2-bottom) [14, 15].

Figure 3 shows the curves of the dependence of the temperature dependences of the relative density of the samples of the compositions in question. As can be seen, the introduction of the second component into zirconium oxide does not lead to a significant change in the final density of the sintered samples, but this value is reached at a higher temperature.

Due to the fact that the particle size in the oxoapatite is larger (Figure 4) than in hydroxyapatite, the density of the sample of ceramics based on zirconium oxide and oxoapatite is greater than in the case of hydroxyapatite (Table 1).

Examination of samples microstructure showed that the addition of apatite powder leads to the appearance of a system of unbranched pores with an average size of 1 × 5 μm, in contrast to ceramics made of zirconium oxide (Figure 5). This indicator is at the lower limit of the optimal pore sizes required for the penetration of cells into the ceramic implant. Uniform distribution of hydroxyapatite in the thickness of zirconium in our opinion is capable of inducing germination of native bone tissue into the implant, thus increasing the strength of the material and not leading to the complete encapsulation of the implant.

Table 2 presents results of the mechanical properties studies of ceramics (Vickers hardness and fracture toughness) in comparison with the corresponding indicators of the most common materials for the manufacture of bioimplants [16].

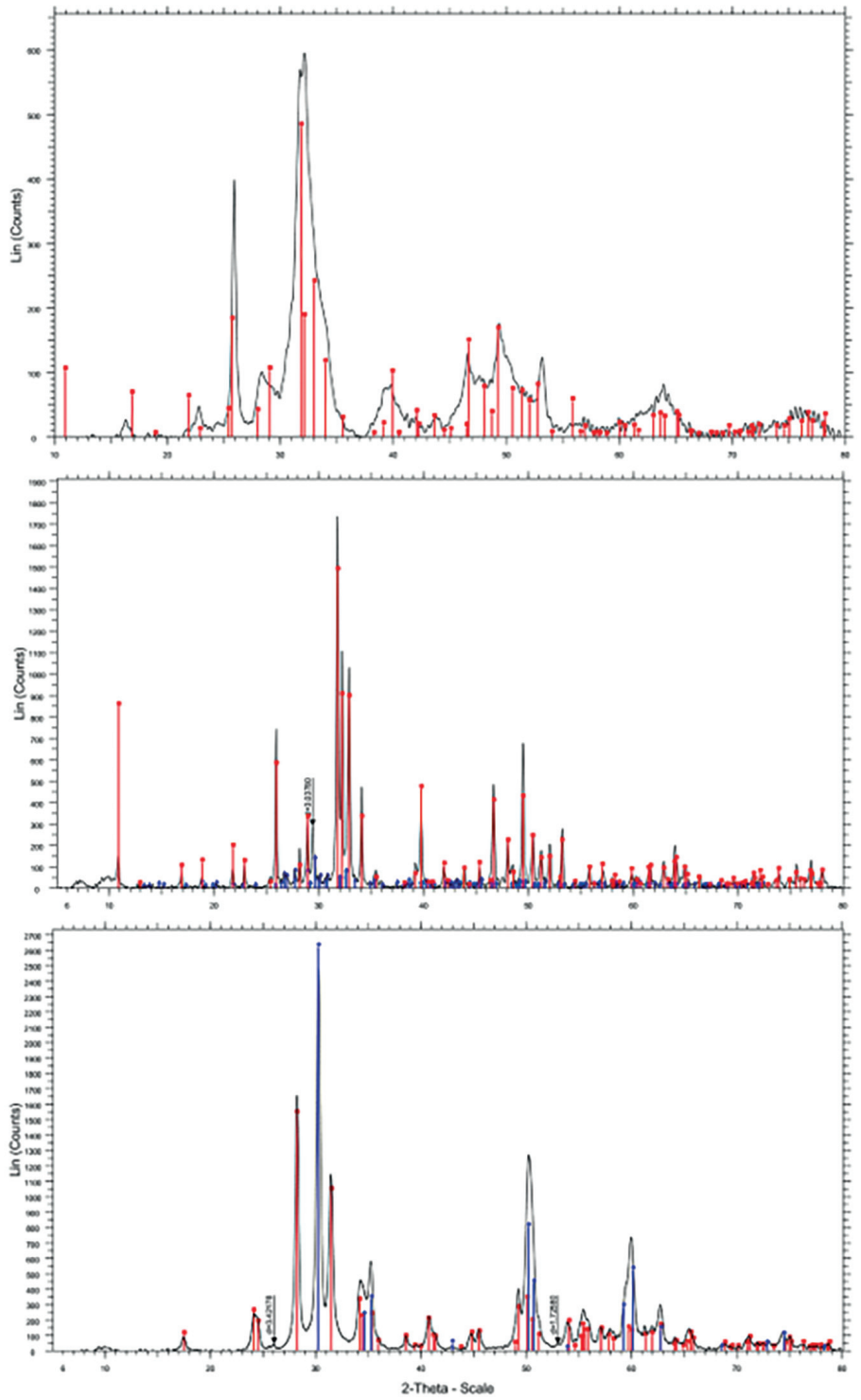

Figure 2. XRD patterns of using compounds: hydroxyapatite (top), oxoapatite (middle): red for oxoapatite, blue for calcium pyrophosphate, zirconium oxide (bottom): blue for tetragonal modification, red for monoclinic modification

Table 2

Strength characteristics of the obtained ceramics in comparison with other biomaterials

	Vickers hardness H_v (GPa)	Crack resistance K_{1C} (MPa·$m^{1/2}$)
ZrO_2 + 20% HAp	11.0(1)	2.9(1)
ZrO_2 + 20% OAp	11.4(1)	3.2(1)
ZrO_2	11.3(1)	3.6(1)
Bioglass 45S5	0.458+/- 9.4	
Glassceramics Cerabone	0.68	2.00
Glassceramics Biovert	0.50	0.5-1.0
Hydroxyapatite (>99,2%)	0.60	1.0

As could be seen, the usage of the composite hydroxyapatite (oxoapatite) / zirconium oxide makes it possible to obtain a material with significantly higher values of hardness and fracture toughness.

Enhanced performance characteristics of biomaterials, in particular hydroxyapatite, can be achieved by introducing 10-30% metal fibers, however, the introduction of metallic fibers in the long-term perspective is undesirable, because that can lead to rejection of the material. In this case biocompatible zirconium oxide is used.

4. Conclusion

The preparation of composites based on apatites and zirconium oxide, thus, solves a number of issues of modern biomaterial science. Firstly, the composition of ceramics includes both biologically inert component (zirconium oxide) and biologically active (compounds with apatite structure), which provides the processes of osteogenesis. Sec-

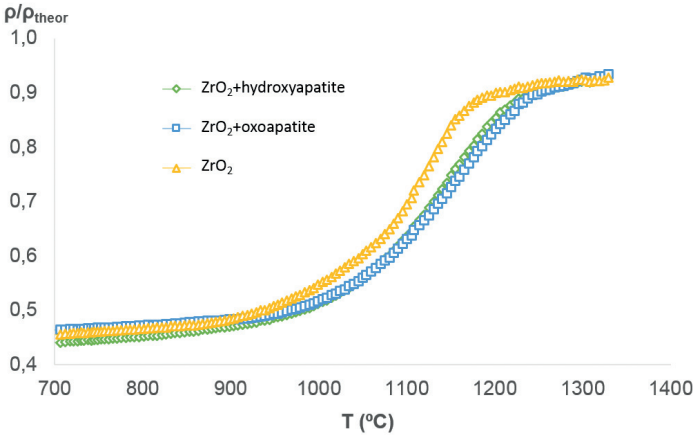

Figure 3. Graph of temperature dependence of relative density of samples during sintering of ceramics

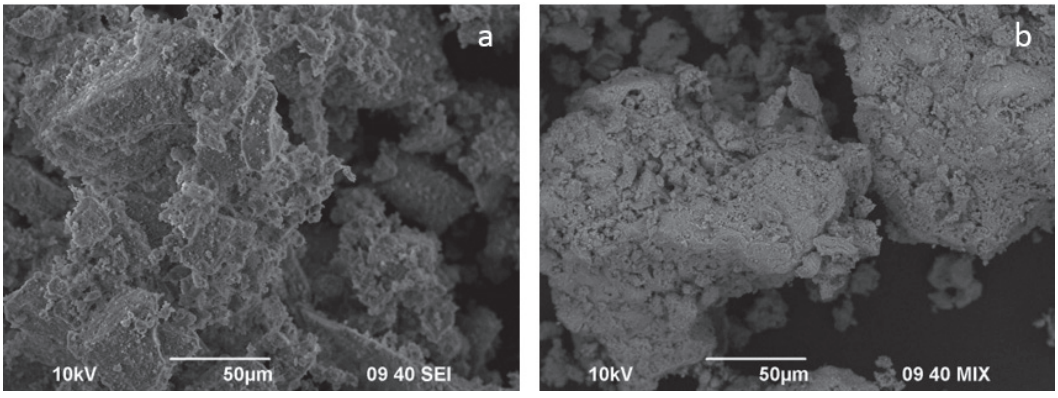

Figure 4. Microimagies of hydroxyapatite (a) and oxoapatite (b)

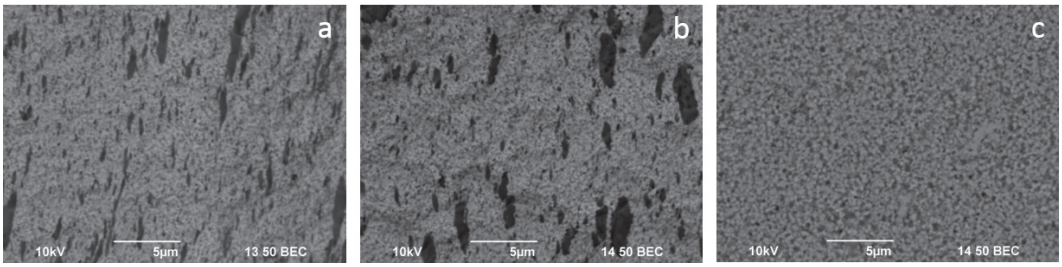

Figure 5. Microimagies of surfaces of ZrO2/HAp (a), ZrO2/OAp (b) and ZrO2 (c) ceramics

Table 1

Sintering modes and characterization of test mixtures

Sample №	**1**	**2**	**3**
Composition	ZrO_2 + 20% HAp	ZrO_2 + 20% OAp	ZrO_2
T_{sint} (°C)	1150		
P_{sint} (MPa)	70		
$V_{heating}$ (°C/min)	RT-600 °C – 100 600-1150°C – 50		
τ_{sint} (min)	0		
Cooling	no		
ρ (g/cm³)	5.579	5.623	6.016
ρ/ρ_{theor} (%) **ρ_{theor} (ZrO_2) = 6.016 g/cm³**	92.74	93.44	100.00

ondly, using zirconium oxide as a kind of matrix in combination with the rapid method of sintering ceramics (SPS), make it possible to solve the problem of low performance properties of materials based on hydroxyapatite. In addition, this approach makes it possible to obtain a pore system in the material necessary for the penetration of cells into the implant.

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