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INFLUENCE OF SINTERING TEMPERATURE AND COMPRESSION SPEED ON PROPERTIES OF HYDROXYAPATITE DISKS

Abstract: The present article is dedicated to an investigation of a production method of hydroxyapatite (HA) disks with a study of an influence of compression speed (5, 10 and 15 mm/min) and sintering temperature (900 °C and 1200 °C) on structure and properties of those disks. Measurements of density, mass loss and shrinkage as well as scanning electron microscopy (SEM) and light optical microscopy (LM) observations were performed. The aim of this study is to define optimal process parameters, which are applicable for using as a substrate for in vitro experiments.

Key words: hydroxyapatite, bio-ceramics, pellets, dense disks, structure, heat treatment

1. INTRODUCTION

Hydroxyapatite demonstrates exceptional biocompatibility, bioresorbability, and tolerance to physiological tissues. Moreover it is referred to as an "intelligent" material due to its ability to respond and adapt to physiochemical environments [1, 19]. Hydroxyapatite finds extensive application in the biomedical sphere: as a coating for a variety of prosthesis and implants [4, 6, 11, 20], as component in bone-forming cells, for bone remodeling [3, 13, 15] and bone grafts [13, 14], tissue engineering scaffolds and eye ball prosthesis [13]. In case of biological studies, hydroxyapatite is used for tooth enamel modelling [2]. Samples for biological studies [7] are produced in form of small disks or pellets. There are few commercial producers of pellets in the USA and Western Europe, one example is Clarkson Chromatography Products, Inc. (USA).

2. RESULTS AND DISCUSSION

2.1. Materials and methods

The HA disks were produced 9.6 mm in diameter and 2.4 mm in high, using a commercially available HA powder with heterogeneous globular-shaped particles of 50 to 200 μm (Fig. 1) and exhibiting a quasi-stoichiometric composition with a Ca/P molar ratio of 1.68. For the investigation, three set of samples were produced each with a different compression speed: 5, 10 and 15 mm/min respectively.

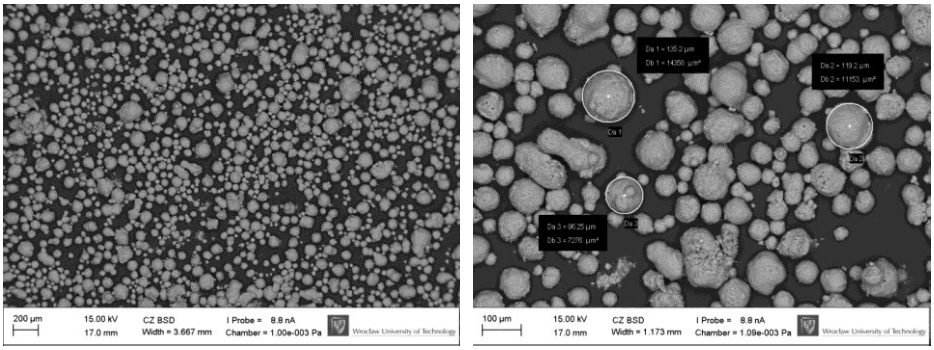

Fig. 1. SEM micrograph showing the particle size distribution of hydroxyapatite

Heat treatment (HT) was performed using high temperature laboratory furnace Czylok FCF 11/160 M without protective atmosphere for the two sintering temperatures: 900°C and 1200°C. For each temperature, a sample group contained 5 pellets with 3 compression speeds. This way 6 sets of the test samples were obtained (at 3 different compression speeds and with 2 different temperatures).

The choice of temperatures for sintering laid on an analytical research [8, 10, 12, 16, 18]. The key factors in the decision were (a) presence of HA phase – analytically proved for every presented temperature (from 900 °C to 1250 °C); (b) interrelation between density and linear shrinkage, (c) mechanical properties as hardness and strength.

The non-destructive 3D analysis of the internal structure (µCT), microscopic observation (LM, SEM) and chemical composition analysis (SEM-EDS, FTIR), evaluation of density and shrinkage (gravimetric analysis) were carried out for clarifying the influence of compression speed and heat treatment on the structure and properties of the HA disks.

2.2. Results and discussion

The micro CT analysis–includes control of porosity level, compression stress marks and cracks) revealed that the closed porosity within the samples was absent or less than 0,001%. Samples had numerous technological defects (scratches due of compression) on the surface as well as are exhibited the footprints of compression stress (Fig. 2).

Visual inspection of the surface showed that the change in compression speed did not influence the surface structure of the disks. Due to the sintering at a higher temperature (1200 °C), the surface color of the pellets changed to shades of gray and blue. According to [5, 9] this might happen in result of an oxidation of Mn^{2+} ions (trace element in the hydroxyapatite) into Mn^{5+} and the formation of MnO_4^{3-} ions. That oxidation of Mn leads to the color changing, from white to grey-blue.

Pellets sintered at 1200 °C were characterized by a cell-type structure (Fig. 3, right image), with grain sizes from 600 nm to ≈3 µm.

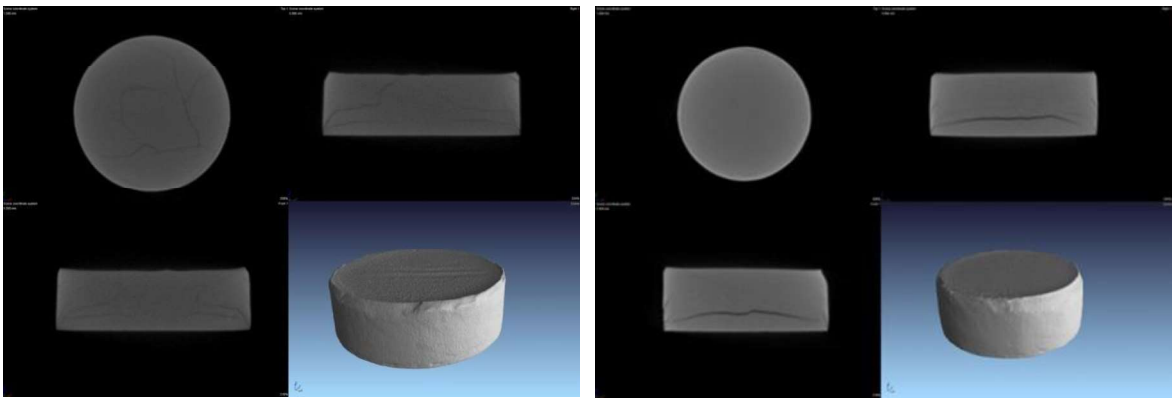

Fig. 2. The results of non-destruction inner structure analyze by computer microtomography (μCT): left - pellet sintered at 900° C, 10 mm/min; right - 1200° C, 10 mm/min

The EDS-SEM analysis showed the presence of typical HA elements (Ca, P, O) in samples of each group (Table 1). The FTIR analysis proved that unheated HA disks, as well as samples after HT at 900 °C, contained hydroxyapatite. Moreover, samples after HT showed more stable (without unstable OH-groups) and structured hydroxyapatite. In the literature could be find data about contaminants in the pellets due to use of spray [17], which is prevent pellets from the sticking with the mold and consequent breaking. In this study, we are avoiding to use any kind of lubrication for keep the pellets free of contamination.

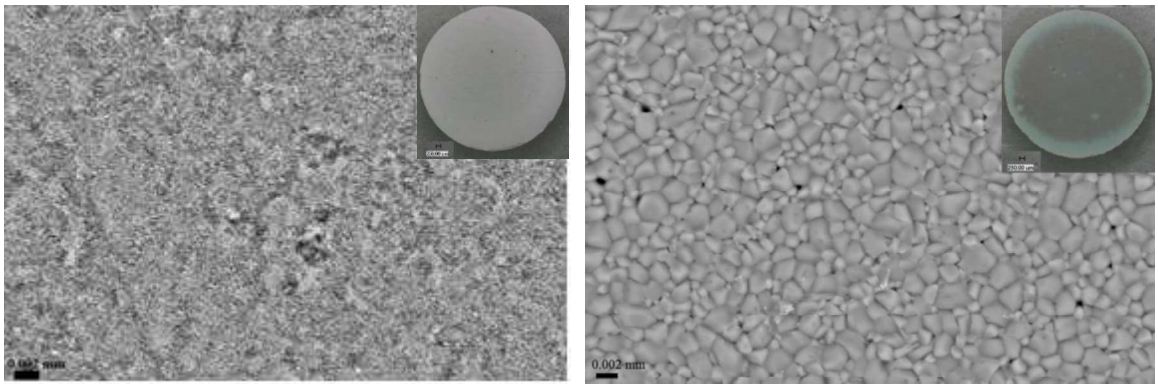

Fig. 3. Structure of the pellet's surface, SEM. Left – 900° C, 10 mm/min; right - 1200° C, 10 mm/min

Table 1. Comparing EDX-analysis results of test samples

Elements by EDX, in wt.%	Ca	P	O	Trace elements
Temperature / Compression speed	**900 °C**			
5 mm/min	42.97	16.39	40.64	Mg ≈1.5
10 mm/min	42.86	16.39	40.75	Cl ≈2; Mg ≈0.15
15 mm/min	41.12	16.03	42.85	Cl ≈1.4; Mg ≈0.12
Temperature / Compression speed	**1200 °C**			
5 mm/min	41.67	15.93	42.39	-
10 mm/min	42.86	16.45	40.69	-
15 mm/min	42.30	16.33	41.37	Optionally, S ≈2.92;

The results of a gravimetric analysis (Fig. 4 a, b) are prove that the properties of the pellets do not meaningfully influenced by compression speed in compare with an influence of sintering temperature. The higher sintering temperature results in higher density and shrinkage.

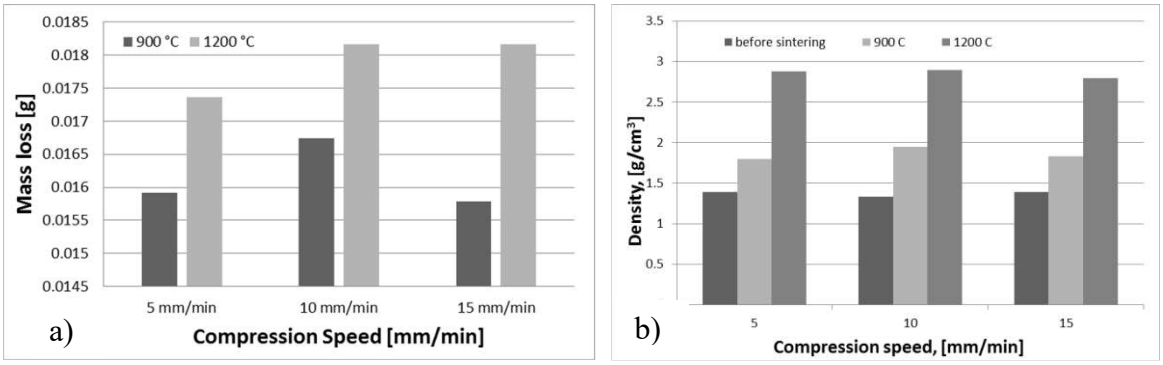

Fig. 4. (a) Mass loss of hydroxyapatite disks after heat treatment;
(b) Mutual influence of compression speed and sintering temperature on density of HA pellets

Data in literature about the relative density of hydroxyapatite disks after sintering are quite contradicting. For example, in [12] the authors claimed that relative density of the test samples after sintering at 1200 °C were ≈96%; contrary to authors of [8] who reported a relative density of ≈78-80% for samples sintered at the same temperature. The relative density from samples presented in this research after sintering at 1200 °C were ≈86-88% (density calculated based on geometric measurements) and up to 91-92% (density evaluation based on volume extrapolation by means of μCT). Those results were comparable with values from analytical study [8, 10, 12, 16, 18], where disks sintered at 1150 °C had a similar density (88%). Such difference could appear due to high level of defects – inner cracks (result of compression stress) and surface defects. It was easy to notice that relative density increased 1.5 times and shrinkage increased 2 times for samples sintered at 1200 °C in compare with samples sintered at 900 °C.

The dependence between sintering temperature, compression speed and its influence of the density of pellets is presented on Fig. 4, b. It is clearly seen, that tendency is the same for various compression speed.

The changes of relative density (Table 2) due to heat treatment and shrinkage were evaluated based on measurements of weight, height and diameter of the test samples. The results presented in Table 2 are following prove that compression speed does not meaningfully influenced on the properties of the pellets in compare with influence of sintering temperature.

Table 2. Changes of relative density and shrinkage (based on geometric measurements)

Compression speed	Relative density, ρ/ρ_o, %			Shrinkage, %	
	Before sintering	900 °C	1200 °C	After 900 °C	After 1200 °C
5 mm/min	44.13	54.81	86.84	7.73	15.55
10 mm/min	42.12	54.80	88.35	7.79	18.23
15 mm/min	44.17	56.01	87.71	11.05	23.94

The applicability for *in vitro* experiments of HA disks was proved in Medical University of Wroclaw [7].

3. CONCLUSIONS

The method of obtaining hydroxyapatite pellets is presented. They are applicable for biological studies, which were proving by *in vitro* experiment [7]. No meaningful influence of compression speed on the structure and properties of hydroxyapatite disks were noticed. The higher temperature of sintering (1200 °C) results in

(a) appearing of a cell structure in samples (similar to the commercially produced samples) with cell/grain size up to 2..2.5 μm;

(b) surface discoloration of the samples (grey and blue shades) due to oxidation of a trace element – manganese;

(c) higher density and shrinkage.

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WPŁYW TEMPERATURY SPIEKANIA I PRĘDKOŚCI ŚCISKANIA NA WŁASNOŚCI KRAŻKÓW HYDROKSYAPATYTOWYCH

Streszczenie: Niniejszy artykuł poświęcony analizie sposobu produkcji krążków hydroksyapatytowych (HA) poprzez ocenę wpływu szybkości ściskania (5, 10 i 15 mm/min) i temperatury spiekania (900 ° C i 1200 ° C) na strukturę i właściwości krążków. Plan badań zawierał pomiary gęstości, utraty masy i kurczliwości oraz obserwację struktury krążków przy użyciu skaningowej mikroskopii elektronowej (SEM) i mikroskopii optycznej (MO). Celem badań jest określenie optymalnych parametrów procesu do produkcji krążków HA, stosowanych jako podłoże dla eksperymentów in vitro.