Article

Powder mixture for the production of microporous ceramics based on hydroxyapatite

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Abstract: Powder mixture with given molar ratio Ca/P = 1.67 consisting of brushite (calcium hydrophosphate dihydrate) $CaHPO_4 \cdot 2H_2O$, calcium oxalate monohydrate $CaC_2O_4 \cdot H_2O$ in form of whewellite and weddellite and some quantity of quasi-amorphous phase was obtained as a result of the interaction of hydroxyapatite powder $Ca_{10}(PO_4)_6(OH)_2$ with an aqueous solution of oxalic acid $H_2C_2O_4$ at a molar ratio of $Ca_{10}(PO_4)_6(OH)_2/H_2C_2O_4$ = 1:4 under mechanical activation conditions. This powder mixture was used to produce microporous monophase ceramics based on hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ with aperient density of 1.25 g/cm^3 after firing at 1200 ^oC. Microporosity of sintered ceramics was formed due to presence of particles with plate-like morphology, restraining shrinkage during sintering. Microporous ceramics based on hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ with roughness of the surface as a consequence of the created microporosity can be recommended as a biocompatible material for the bone defects treatment and as a substrate for bone cell cultivation.

Keywords: hydroxyapatite; oxalic acid; powder, whewellite, weddellite, calcium oxalate monohydrate, brushite, calcium hydrophosphate dihydrate, heterophase reaction, ceramics, microporosity

1. Introduction

The creation of ceramic materials based on calcium phosphates is one of the intensively developing areas of modern materials science for medicine [1]. These materials are biocompatible and can be used in medicine as a porous matrices for replacing lost or damaged bone tissue or as substrates for cell cultivation. Ceramics based on hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) are widely used as material for bone implants creation due to its stability and the similarity of chemical and phase compositions of inorganic part of natural bone [2,3].

Ceramics for bone implants have to be porous with at least two levels of porosity to mimicking the natural bone. Macro pores have to be not less than 100 µm and the dimension of micro pores should be about 10 µm [4, 5].

Microporosity of ceramics giving roughness to the surface can improve biointegration and osteoconductivity of material and ensure effective fixation and reproduction of bone tissue cells, as well as fusion of the implant with the body [6].

Ceramics based on hydroxyapatite are very often prepared from HA powder previously synthesized by various methods. The simplest and most common way to obtain hydroxyapatite powder is its precipitation from an aqueous solution of the corresponding substances, which are phosphoric acid or soluble phosphates of ammonium, sodium, potassium as phosphate ion sources and, soluble calcium salts (acetate, nitrate, chloride) as calcium ion sources [7, 8]. Another way to prepare HA powders or ceramics consisted in heat treatment of preliminarily homogenized powder mixtures of different salts with the preset molar ratio of Ca/P = 1.67 [9].

To create microporosity one can use special thermal treatment scheduler to get undersintered ceramic material [10] or specially via sol-gel synthesis prepared powder system [11]. Another method of microporosity creation consists in using organic [12, 13] or inorganic [14, 15] additives in form of particles with a small dimensions as a sacrificed porogens. Special additives which have ability to decompose with the release of a sufficiently large volumes of gases at different stages of ceramics production can be used to generate microporosity. CO_2, NH_3 from NH_4CO_3 can be used for example at the stage of slurry preparation [16] or CO_2 from sodium of potassium carbonates in presence of melt can be used at the stage of heat treatment [17] for creation of microporosity of material.

In the present work for preparing of microporous HA-ceramics we used intentionally prepared powder mixture including particles with the plate-like morphology expecting that particles with this form would restrain sintering.

The purpose of this work consisted in preparing and investigation of powder mixture with preset molar ratio Ca/P=1,67 including plate-like particles which able to restrain shrinkage during sintering of HA-ceramics for microporosity creation. To prepare powder mixture with preset molar ratio Ca/P=1,67 powder of HA was treated in water solution of oxalic acid $H_2C_2O_4$ under mechanical activation conditions. We expected that interaction of basic calcium phosphate salt ($Ca_{10}(PO_4)_6(OH)_2$, HA) with water solution of oxalic acid $H_2C_2O_4$ give us opportunity to prepare powder mixture including brushite (calcium hydrophosphate dihydrate) $CaHPO_4·2H_2O$ and calcium oxalate monohydrate $CaC_2O_4·H_2O$.

2. Materials and Methods

To obtain powder mixture including calcium hydrophosphate dihydrate (brushite) $CaHPO_4·2H_2O$ and calcium oxalate monohydrate $CaC_2O4·H_2O$, powders of HA $Ca_{10}(PO_4)_6(OH)_2$ (CAS No. 1306-06-5, puriss. p.a. ≥ 90%, RiedeldeHaen, Sigma-Aldrich Laborchemikalien, 04238, lot 70080, Germany) and oxalic acid dihydrate $H_2C_2O_4·2H_2O$ (grade "pure", GOST 22180-76) were used. These powders were taken in a molar ratio of $Ca_{10}(PO_4)_6(OH)_2/H_2C_2O_4$ = 1:4. The following reaction (1) were used for calculation of quantity of starting powders:

$$Ca_{10}(PO_4)_6(OH)_2 + 4H_2C_2O_4·2H_2O + 6H_2O = 4CaC_2O_4·H_2O + 6CaHPO_4·2H_2O \quad (1)$$

5.02 g of oxalic acid dihydrate $H_2C_2O_4·2H_2O$ powder, 10.00 g of HA $Ca_{10}(PO_4)_6(OH)_2$ powder and 55 g of grinding media (balls based on ZrO_2-ceramics) were places in agate vessel. 40 ml of distilled water was added to the resulting mixture. The vessel was installed in a planetary mill. The treatment of HA $Ca_{10}(PO_4)_6(OH)_2$ powder in water solution of oxalic acid $H_2C_2O_4$ (1 M) was conducted for 15 min in a planetary mill (Fritch Pulverisette, Germany) at rotation speed of 500 rpm. Then the resulting suspension was placed into porcelain cup and dried in air for a week until the water completely evaporated.

Pre-ceramic powder compacts in the form of discs with a diameter of 12 mm and a height of 2-3 mm were made from prepared powder mixture using a manual press (Carver Laboratory Press model C, USA) at 100 MPa using a steel mold. Then the samples were fired in a furnace at 500 °C, 1000 °C, 1100 °C and 1200 °C with exposure at the specified temperatures for 2 hours (the heating rate of the furnace was 5 °C/min). The mass, linear dimensions of the samples were measured before and after firing. Then linear shrinkage and density of samples were calculated. Prepared powder mixture was additionally heat treated at 200 °C with exposure at this temperature for 30 minutes (the heating rate of the furnace was 5 °C /min) for better understanding of processes of transformation of phase composition of powder system under heating.

The phase composition of the powder mixture after treatment in a planetary mill and after heat treatment at 200 ^oC as well as ceramic samples after firing was determined by X-ray powder diffraction (XRD) analysis on a Rigaku D/Max-2500 diffractometer (Japan) with a rotating anode, using Cu–Ka radiation (average wavelength λ = 1.54183 Å), accelerating voltage 50 kV, tube current 250 mA, angle interval 2Θ: from 2° to 70°, step 2Θ -

0.02°, speed 4°/min). Phase analysis was performed using ICDD PDF2 database [18] and Match!3 software (https://www.crystalimpact.com/).

Prepared powder mixture after drying was examined by synchronous thermal analysis (TA), which was performed on a NETZSCH STA 449 F3 Jupiter thermal analyzer (NETZSCH, Germany) at a heating rate of 10 °C/min. The mass of the sample was at least 10 mg. The composition of the gas phase formed during the heating of powder mixture was studied using a quadrupole mass spectrometer QMS 403 Quadro (NETZSCH, Germany) combined with a thermal analyzer NETZSCH STA 449 F3 Jupiter. Mass spectra (MS) were recorded for the mass numbers 18 (H_2O); 44 (CO_2).

Powder mixture after treatment in a planetary mill and ceramics after firing were examined by scanning electron microscopy (SEM) on LEO SUPRA 50VP electron microscope (Carl Zeiss, Germany; auto-emission source). This investigation was carried out at an accelerating voltage of 3-20 kV in secondary electrons (SE2 detector). The surface of the samples was coated with a layer of chromium (up to 10 nm).

3. Results and Discussion

According to the XRD data (Figure 1), the phase composition of powder mixture obtained as a result of the interaction of HA $Ca_{10}(PO_4)_6(OH)_2$ powder with a 1M water solution of oxalic acid $H_2C_2O_4$ under mechanical activation condition and drying in air for a week consisted of brushite (calcium hydrophosphate dihydrate) $CaHPO_4{\cdot}2H_2O$ and calcium oxalate monohydrate $CaC_2O_4{\cdot}H_2O$ in form of whewellite (PDF card 20-231) and weddellite (PDF card 17-541).

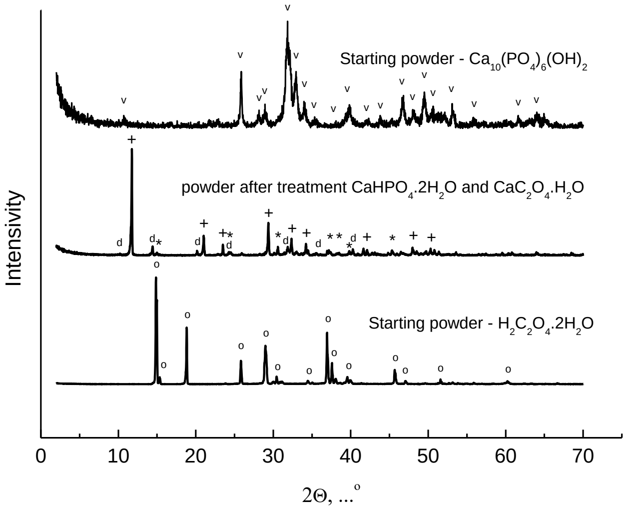

Figure 1. XRD data for starting components and resulting powder mixture: v - $Ca_{10}(PO_4)_6(OH)_2$ (PDF card 9-432); o - $H_2C_2O_4{\cdot}2H_2O$ (PDF card 14-832); + - $CaHPO_4{\cdot}2H_2O$ (PDF card 9-77); * - $CaC_2O_4{\cdot}H_2O$ (PDF card 20-231); d - $CaC_2O_4{\cdot}H_2O$ (PDF card 17-541).

The XRD data confirmed that reaction (1) took place during treatment in planetary mill and drying of suspension. According to Match!3 software (https://www.crystalimpact.com/) phase composition of prepared powder mixture consisted of brushite $CaHPO_4{\cdot}2H_2O$ (Entry number 96-231-0527, 84.1 %) [19] and weddellite $CaC_2O_4{\cdot}2.2H_2O$ (Entry number 96-231-0999, 15,9 %) [20]. Additionally, the Match! Phase Analysis Report marked 30% as unidentified peak area. Phase composition of prepared powder mixture determined by using different programs are in good correlation. It should be noted that some quasi-crystalline phases not detected via XRD could form during interaction of HA $Ca_{10}(PO_4)_6(OH)_2$ powder with water solution of oxalic acid $H_2C_2O_4$.

Figure 2 shows a micrographs of a powder mixture obtained as a result of the interaction of HA $Ca_{10}(PO_4)_6(OH)_2$ powder with an 1M water solution of oxalic acid $H_2C_2O_4$ under conditions of mechanical activation and drying in air during 1 week. On the micrograph, one can see two kinds of particles: particles of a plate-like morphology with dimensions about 10-20 mm (Figure 2, a) and particles of isometric morphology and dimensions up to 100 nm. The plate-like morphology is inherent to brushite $CaHPO_4{\cdot}2H_2O$ according to scientific literature data and our experience [21]. So, we could assume that particles with isometric morphology and dimensions up to 100 nm were weddellite or whewellite (calcium oxalate monohydrate) $CaC_2O_4{\cdot}H_2O$. One can see that these isomeric particles presented in powder as aggregates with dimensions of 500-1000 nm and as individual particles on the surface of plate-like brushite $CaHPO_4{\cdot}2H_2O$ particles.

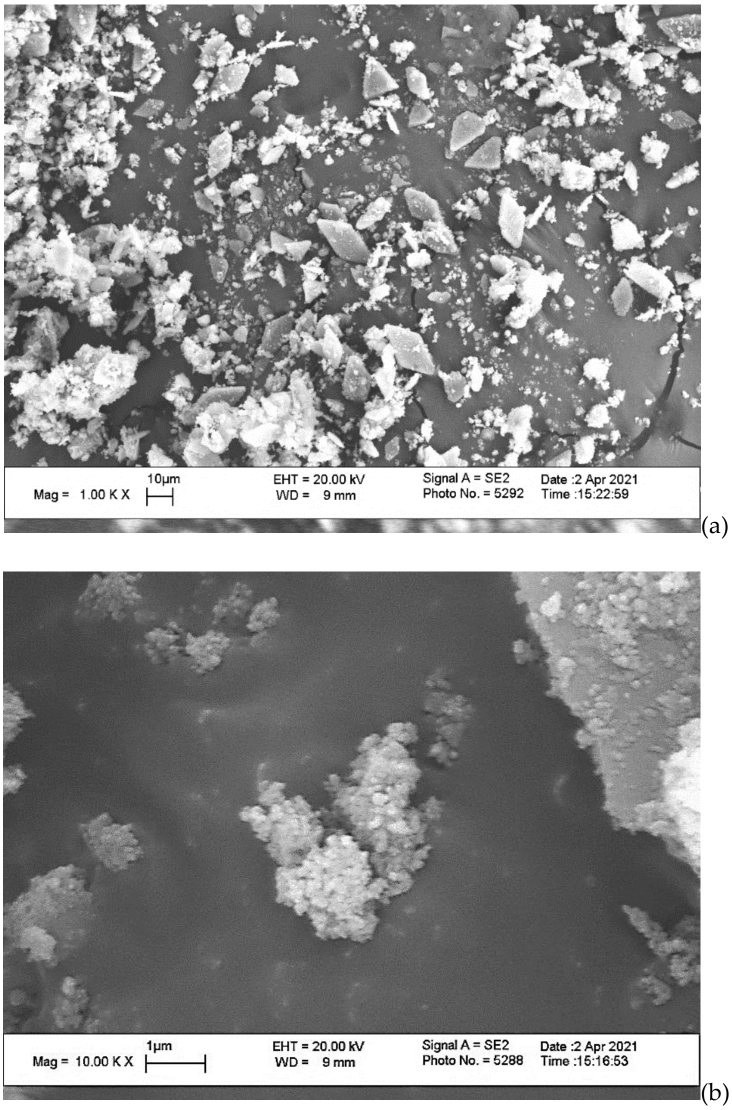

Figure 2. SEM images of the powder mixture obtained by the interaction of HA powder $Ca_{10}(PO_4)_6(OH)_2$ with a water solution of oxalic acid $H_2C_2O_4$ under mechanical activation after drying in air for a week: x1000 (a) and x 10000 (b).

Figure 3 shows the data of synchronous thermal analysis: thermogravimetry (TG) and differential scanning calorimetry (DSC) curves for the studied powder mixture when heated from 40 °C to 1000 °C. Figure 4 shows the mass spectra of evolving gases with m/Z = 18 (H_2O) and m/Z = 44 (CO_2) resulting from the thermal decomposition of components of the powder mixture. The total mass loss of the powder mixture when heated up to 1000 ^oC was 33%. It should be noted that if powder mixture consisted only from product formed according reaction (1) the total mass loss according calculation would be 42%. This fact can additionally points on possible presence of non-detected by means of XRD less hydrated quasi-amorphous products formed during treatment of HA $Ca_{10}(PO_4)_6(OH)_2$ powder in water solution of oxalic acid $H_2C_2O_4$ in the condition of mechanical activation. There are 3 noticeable steps on the curve of mass loss. The mass loss at the first step is estimated as 14% (90 – 300 °C), at the second step - 10 % (300-550 °C) and at the third step - 9 % (550-750 °C).

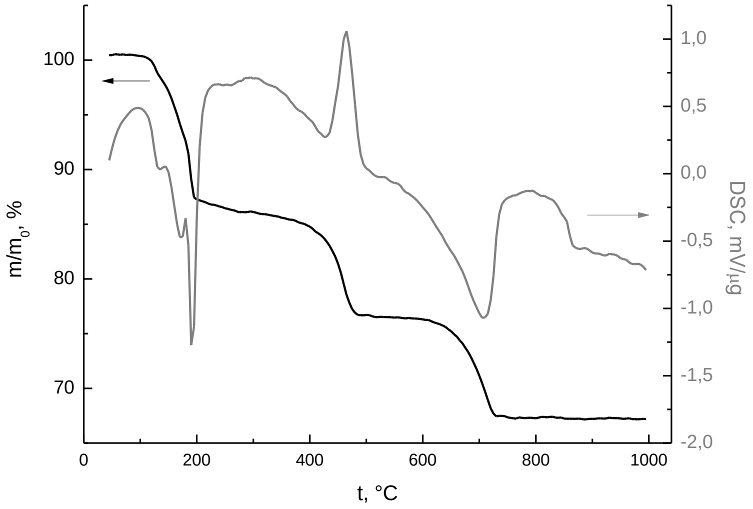

Figure 3. The results of synchronous thermal analysis (TA): thermogravimetry curves (TG, in black) and differential scanning calorimetry (DSC, in gray).

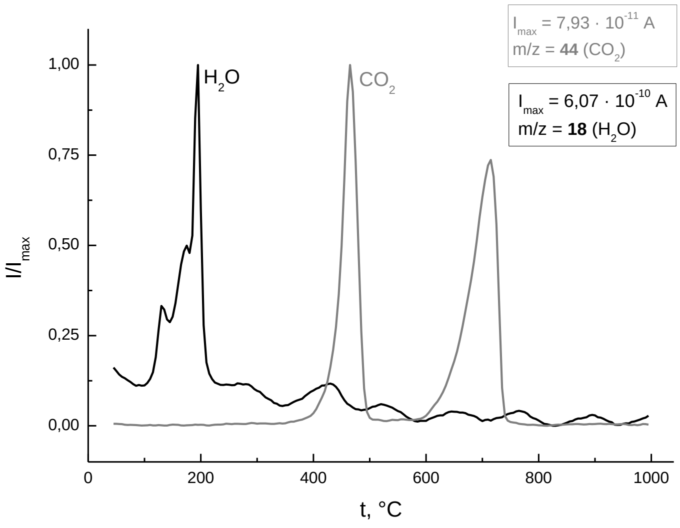

Figure 4. Mass spectra for evolving gases with m/Z=18 (in black) and m/Z=44 (in grey). Curves were normalized with respect to Imax = $6.07 \cdot 10^{-10}$ A for H_2O (m/Z = 18) and to Imax = $7.93 \cdot 10^{-11}$ A for CO_2 (m/Z = 44).

There are 3 endo-peaks on the DSC curve in the first temperature interval (130 °C, 173 °C, and 192 °C). In the mass spectrum curve for m/Z = 18 (H_2O) in this range of 90 – 300 °C one can see 3 peaks at the same temperatures. Thermal decomposition of whewellite/weddellite $CaC_2O_4 \cdot H_2O$ and brushite $CaHPO_4 \cdot 2H_2O$ can take place in this range of temperatures according to reactions (2) and (3) respectively with the formation of anhydrous calcium oxalate CaC_2O_4 and monetite $CaHPO_4$.

$$CaC_2O_4 \cdot H_2O = CaC_2O_4 + H_2O \tag{2}$$

$$CaHPO_4{\cdot}2H_2O = CaHPO_4 + 2H_2O \quad (3)$$

According to scientific literature data thermal decomposition of $CaC_2O_4{\cdot}H_2O$ (reaction (2)) takes place at 167.9 °C [22] and thermal decomposition of brushite $CaHPO_4{\cdot}2H_2O$ takes place at 200 °C (reaction (3)) [23]. It should be noted that simulations presence of these two hydrated salts can influence on thermal decomposition processes of each of them. Probably the mass loss at 130 °C can be explained with possible interaction of these two hydrated calcium salts. Also, this peak may reflect the process of thermal transformation of any undetected by XRD quasi-amorphous phase presence of which estimated as possible. After heat treatment at 200 °C according to XRD data (Figure 5, Table 1) the following phases were detected in the powder mixture: $CaHPO_4$, $Ca_3(PO_4)_2{\cdot}xH_2O$, $CaC_2O_4{\cdot}H_2O$. The presence of $CaC_2O_4{\cdot}H_2O$ in powder mixture indicates the incompleteness of the thermal decomposition process according to reaction (2). The form of the XRD curve (Figure 5) indicates that a remarkable part of the powder mixture under investigation presents in quasi-amorphous form after heat treatment at 200 °C.

The second noticeable step on the curve of mass loss is in the temperature interval of 300-550 °C (Figure 3). At mass spectra for m/Z=44 in this interval there is a peak (465 °C) reflecting CO_2 evolving. The thermal decomposition of anhydrous calcium oxalate CaC_2O_4 with formation of calcium carbonate $CaCO_3$ takes place with the release of heat (DSC curve, Figure 3) according to reaction (4) [22, Chang].

$$CaC_2O_4 + 1/2O_2 = CaCO_3 + CO_2 \quad (4)$$

Grey color of the samples after firing at 500 °C give us opportunity to conclude about presence of some quantity of amorphous carbon in the powder compact. In the temperature range from 400 °C to 450 °C, monetite $CaHPO_4$ undergoes dehydration with the formation of calcium diphosphate γ-$Ca_2P_2O_7$ (reaction (5), which is confirmed by a peak (425 °C) on the mass spectrum curve (Figure 4, m/Z = 18).

$$2CaHPO_4 = \gamma\text{-}Ca_2P_2O_7 + H_2O \quad (5)$$

XRD data after heat treatment at 500 °C (Figure 5, Table 1) confirm presence of calcium carbonate $CaCO_3$ in form of calcite and γ-calcium pyrophosphate γ-$Ca_2P_2O_7$ in the phase composition of samples. Simultaneous presence at powder system of calcium carbonate $CaCO_3$ and calcium pyrophosphate $Ca_2P_2O_7$ makes it possible the formation of tricalcium phosphate $Ca_3(PO_4)_2$ or hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ according to reactions (6) and (7). Tricalcium phosphate $Ca_3(PO_4)_2$ can form due to thermal decomposition of hydrated tricalcium phosphate $Ca_3(PO_4)_2\ xH_2O$ (analog of Ca-deficient HA – $Ca_9(HPO_4)(PO_4)_5(OH)$) (reaction (8) and (9). Moreover, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ can form from tricalcium phosphate $Ca_3(PO_4)_2$ and calcium carbonate $CaCO_3$ according reaction (10).

$$CaCO_3 + Ca_2P_2O_7 = Ca_3(PO_4)_2 + CO_2 \quad (6)$$

$$4CaCO_3 + 3Ca_2P_2O_7 + H_2O = Ca_{10}(PO_4)_6(OH)_2 + 4CO_2 \quad (7)$$

$$Ca_3(PO_4)_2\ xH_2O = Ca_3(PO_4)_2 + xH_2O \quad (8)$$

$$Ca_9(HPO_4)(PO_4)_5(OH) = 3Ca_3(PO_4)_2 + H_2O \quad (9)$$

$$3Ca_3(PO_4)_2 + CaCO_3 + H_2O = Ca_{10}(PO_4)_6(OH)_2 + CO_2 \quad (10)$$

These reactions (6), (7) and (10) can explain the CO_2 evolving (peak at 715 °C, Figure 4) in the third noticeable step at mass loss curve in the interval 550-750 °C (Figure 3). As one can see no mass changes were detected during heating in the interval 750-1000 °C in the TG curve.

Figure 5 shows the XRD data of powder mixture after heat treatment at 200 °C and ceramic samples based on powder mixture prepared from powder of HA $Ca_{10}(PO_4)_6(OH)_2$ and oxalic acid dihydrate $H_2C_2O_4{\cdot}2H_2O$ after firing at 500 °C, 1000 °C, 1100 °C and 1200 °C. Table 1 briefly summarizes phase transformations in powder system under investigation from starting powder mixture ($CaHPO_4{\cdot}2H_2O$, $CaC_2O_4{\cdot}H_2O$, non-identified phase quasi-amorphous phase) to final monophase HA ($Ca_{10}(PO_4)_6(OH)_2$) ceramics. Phase composition of ceramics after firing at 1000 °C included HA ($Ca_{10}(PO_4)_6(OH)_2$), β-tricalcium phosphate β-$Ca_3(PO_4)_2$, and small quantity of calcite $CaCO_3$. The presence of β-tricalcium phosphate β-$Ca_3(PO_4)_2$ after firing at 1000 °C can be explained with possibility of reaction (6) in the 550-770 °C interval and reaction (9) and (10) describing transformation of hydrated tricalcium phosphate (as it described in PDF card 18-303) or Ca-deficient hydroxyapatite $Ca_9(HPO_4)(PO_4)_5(OH)$ to the β-tricalcium phosphate β-$Ca_3(PO_4)_2$ which is possible in the 650-800 °C interval [24, 25].

$$Ca_3(PO_4)_2{\cdot}xH_2O = Ca_3(PO_4)_2 + xH_2O \tag{9}$$

$$Ca_9(HPO_4)(PO_4)_5(OH) = 3Ca_3(PO_4)_2 + H_2O \tag{10}$$

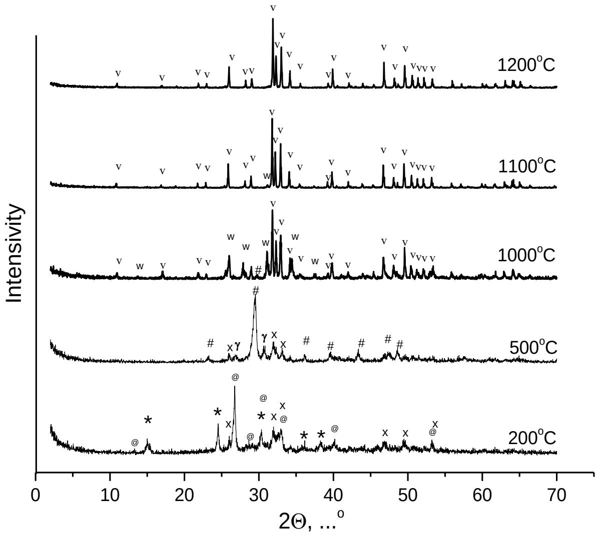

Figure 5. XRD data for powder mixture (200 °C) and ceramic samples (500 °C, 1000 °C, 1100 °C and 1200 °C) after firing: v – $Ca_{10}(PO_4)_6(OH)_2$ (PDF card 9-432); w – β-$Ca_3(PO_4)_2$ (PDF card 9-169); "#" - $CaCO_3$ (PDF card 5-586), * - $CaC_2O_4{\cdot}H_2O$ (PDF card 20-231); @ - $CaHPO_4$ (PDF card 9-80); x - $Ca_3(PO_4)_2{\cdot}xH_2O$ (PDF card 18-303); γ – γ-$Ca_2P_2O_7$ (PDF card 17-499).

Phase composition of ceramics after firing at 1100 °C included HA ($Ca_{10}(PO_4)_6(OH)_2$) and small quantity of β-tricalcium phosphate β-$Ca_3(PO_4)_2$. And finally phase composition of ceramics after firing at 1200 °C included the only phase - HA ($Ca_{10}(PO_4)_6(OH)_2$).

Table 1. Phase composition of powder mixtures and ceramic samples.

After mill	200 °C	500 °C	1000 °C	1100 °C	1200 °C
$CaHPO_4{\cdot}2H_2O$ non-identified phase $CaC_2O_4{\cdot}H_2O$	$CaHPO_4$ $Ca_3(PO_4)_2{\cdot}xH_2O$ $CaC_2O_4{\cdot}H_2O$	γ-$Ca_2P_2O_7$ $Ca_3(PO_4)_2\ xH_2O$ $CaCO_3$	$Ca_{10}(PO_4)_6(OH)_2$ β-$Ca_3(PO_4)_2$ $CaCO_3$ *	$Ca_{10}(PO_4)_6(OH)_2$ β-$Ca_3(PO_4)_2$ *	$Ca_{10}(PO_4)_6(OH)_2$

* - small quantity

XRD data of samples after heat treatment at different temperatures shows that formation of single-phase HA-ceramics from multi-components homogenized powder mixture took place as complicated sequence of different heterogeneous reactions, including thermal decomposition reactions and solid-state reactions. As it is knowing from the scientific literature heterophase reactions can take place during firing and accompany sintering process of HA-ceramics [26, 27]. Investigation presented in this article emphasizes the importance of the preset Ca/P=1,67 molar ratio in starting powder mixture when preparing ceramics based on HA. Presetting of Ca/P=1,67 in starting powder mixture in this work was guaranteed both by high quality of HA powder used and by preparation of powder mixture in via acid-base reaction in mechanical activation condition. This method excludes changes in preset Ca/P molar ratio due to difference in solubility of starting components or influence of pH on preferability of formation of one or other phases as it would possible in case of precipitation of calcium phosphate powders from solutions.

Micrograph of the surface of the ceramic sample based on powder mixture including brushite (calcium hydrophosphate dihydrate) $CaHPO_4 \cdot 2H_2O$ and calcium oxalate monohydrate $CaC_2O_4 \cdot H_2O$ in form of whewellite and weddellite after firing at 1200 °C is presented at Figure 6. Microstructure of ceramic sample fired at 1200 °C consisted of polycrystalline plate-like particles with dimensions 5-15 μm, arched groups of particles 0,5-2 μm, and two kinds of pores with dimensions about 10 and 1-2 μm. Obviously microstructure of HA-ceramics inherits microstructure of starting powder mixture. It can be assumed that formation of phase of HA was realized both on the surface of nano sized particles of calcium oxalate/calcium carbonate and on the surface of micro sized plate-like particles of brushite/monetite/calcium pyrophosphate.

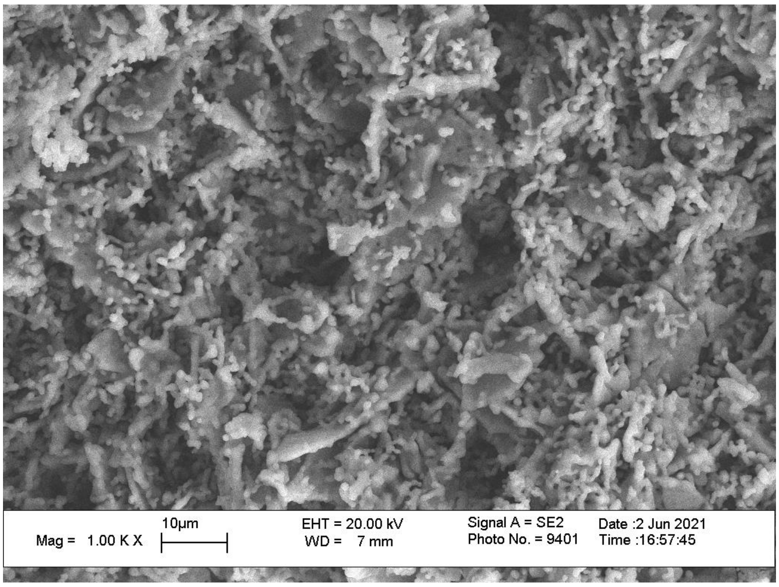

Figure 6. Micrograph of the surface of the ceramic sample based on powder mixture including brushite (calcium hydrophosphate dihydrate) $CaHPO_4 \cdot 2H_2O$, calcium oxalate monohydrate $CaC_2O_4 \cdot H_2O$ in form of whewellite and weddellite and non-identified phase after firing at 1200 °C.

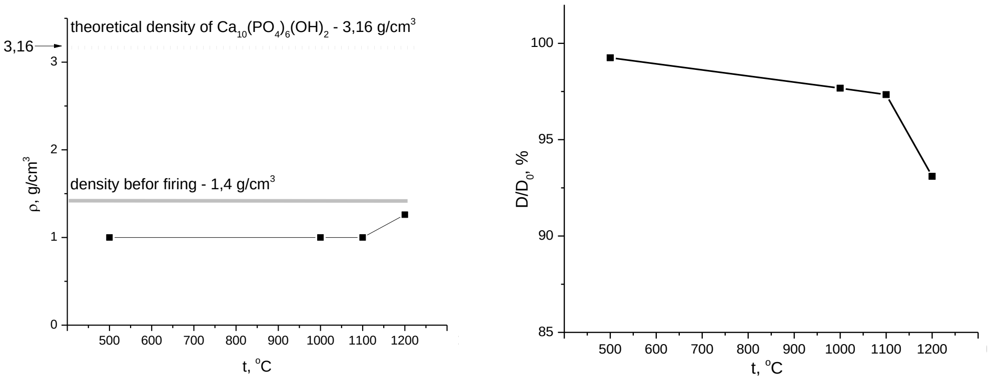

Figure 7. Apparent density (g/cm^3) and relative diameter (D/D$_0$, %) of ceramic samples base on powder mixture ($CaHPO_4 \cdot 2H_2O$, $CaC_2O_4 \cdot H_2O$, non-identified quasi-amorphous phase) after firing at different temperatures.

Apparent density (g/cm^3) and relative diameter (D/D$_0$, %) of ceramic samples after firing at different temperatures are presented at Figure 7. Linear shrinkage increased very slowly from 1% at 500 oC up to 2,7% at 1100 ^{o}C and reach the maximum 7 % at 1200 ^{o}C. Liner shrinkage of HA-ceramics based on uniform synthetic HA powders consisted of isometric particles could reach about 20% [28] or even more than 20% [29,]. Ceramic samples prepared from powder mixture ($CaHPO_4 \cdot 2H_2O$, $CaC_2O_4 \cdot H_2O$, non-identified quasi-amorphous phase) had the maximum density 1.25 g/cm^3 (~ 40 % relatively theoretical density of HA) after firing at 1200 ^{o}C. So, microstructure of HA-ceramics (Figure 6), data of apparent density and relative diameter after firing (Figure 7) confirm possibility to created microporosity via using of powder mixture with plate-like particle restraining shrinkage during sintering.

4. Conclusions

Powder mixture with given molar ratio Ca/P = 1.67 consisting of plate-like particles of brushite (calcium hydrophosphate dihydrate) $CaHPO_4 \cdot 2H_2O$; nanosized isometric particles of calcium oxalate monohydrate $CaC_2O_4 \cdot H_2O$ in form of whewellite and weddellite; and some quantity of non-identified quasi-amorphous phase was obtained as a result of the interaction of HA powder $Ca_{10}(PO_4)_6(OH)_2$ with an aqueous solution of oxalic acid $H_2C_2O_4$ at a molar ratio of $Ca_{10}(PO_4)_6(OH)_2/H_2C_2O_4$ = 1:4 under mechanical activation conditions. This powder was used for creation of microporous monophase HA $Ca_{10}(PO_4)_6(OH)_2$ ceramics. Components of prepared powder mixture with preset Ca/P=1.67 molar ratio take part both in sequences of thermal transformations such as dehydration and decomposition and then in sequences of hetero phase reactions leading to final and target phase composition of ceramics presented by HA $Ca_{10}(PO_4)_6(OH)_2$. It was shown that plate-like particles presented in the powder used for ceramic creation can restrain sintering process and provide the formation of microporosity of HA $Ca_{10}(PO_4)_6(OH)_2$. ceramics.

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