



Reaction sintering in compacted hydrolysed carbonated calcium phosphate

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Abstract

The thermal behaviour of the compact of an uncalcined hydrolysed carbonated calcium phosphate powder slowly heated in air (i.e. under conditions of the reaction sintering) was studied to reveal the reactions which could influence its densification up to 1100 °C. A number of different reactions were found which occurred with different efficiency, but finally enabled a densification of about 94 %TD of the composite with a hydroxyapatite/ β -tricalcium phosphate (HA/ β -TCP) ratio of 48/52. Such composites are highly perspective for further densification under the conventional or other suitable sintering methods at a desired temperature in the production of improved HA/ β -TCP ceramics.

Keywords: bioceramics, biphasic calcium phosphates, reaction sintering, densification

1. Introduction

Biphasic calcium phosphate (BCP) ceramics, consisting of hydroxyapatite (HA), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and β -tricalcium phosphate (β -TCP), $\text{Ca}_3(\text{PO}_4)_2$, have been widely used for bone replacement for more than 20 years and are commercially available. Various applications in clinical medicine revealed both their indisputable advantages and some disadvantages compared to similar calcium phosphate (CP) biomaterials [1–3]. Their drawbacks mainly result from the BCP fabrication. The most widespread preparation is based on the sintering of powder compacts of a wet-chemically synthesized calcium-deficient hydroxyapatite, $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ (CDHA, $1.5 < \text{Ca/P} < 1.67$), at temperatures above 1150 °C. Below this temperature, CDHA decomposes into HA and β -TCP, and the ceramics are sintered from the biphasic HA/ β -TCP mixture. The HA/ β -TCP ratio in the mix-

ture depends on the x value [1–3]. The two components are sintered in different ways. An acceptable HA ceramics with satisfactory density and mechanical properties needs sintering at about 1200 °C. However, the second component, β -TCP, transforms into the high temperature polymorph α -TCP above 1125 °C with about 7% volume expansion which inhibits further densification because of the appearance of cracks in the sintering body. Additionally, as a metastable phase, α -TCP does not completely transform into β -TCP during cooling from the sintering temperature without special additional treatments, so that a three-phase ceramics with unpredictable phase ratio and functional characteristics is usually obtained [4].

Two main approaches are used to overcome these drawbacks. The first approach is based on shifting the TCP transition to a higher temperature, i.e. above the sintering temperature, by introducing various ionic dopants (e.g. MgO, ZnO) into BCP. In the second approach, unconventional techniques, such as microwave sintering or spark plasma sintering, are used [4–7]. Despite some positive results, the indicated approaches

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considerably complicate the BCP ceramics production and, consequently, their availability. Hence, the development of a simple, easy and accessible processing of BCP ceramics is still required.

In the present study, the known but rarely used and weakly studied reaction sintering (RS) [8–13] is applied. Thus, X-ray amorphous/nanocrystalline CP powder was obtained from a carbonated hydrolysis and BCP ceramics of controlled composition was effectively prepared for the first time using RS at temperatures up to 1100 °C.

II. Experimental

A primary amorphous calcium phosphate (ACP) powder with Ca/P = 1:1 was prepared by a modification of the established wet synthesis method, developed by Hayek and Stadlmann [14,15]. The subsequent hydrolysis of the powder to the Ca/P ratio of CDHA was accomplished according to the procedure published in our previous work [16], however, with one substantial alteration. The aim of the previous study [16] was the preparation of an ACP with Ca/P = 1.5 to obtain the metastable α -TCP polymorph after its crystallization. To prepare an initial CP powder with a higher Ca/P ratio in the CDHA range, the hydrolysis was conducted under all other conditions of study [16], but in water carbonated by CO₂ gas bubbling during the entire process. Because the CO₃²⁻ ions formed from dissolved CO₂ effectively substitute HPO₄²⁻ [17], the hydrolysis resulted in a carbonated CP (CCP) with a Ca/P ratio above 1.5 that increased during the hydrolysis.

The obtained CCP powder was uniaxially pressed into pellets at 100 MPa. Before heating (sintering), the pellets were not subjected to preliminary calcination (uncalcined CCP pellets, UCCPs). As a result, the UCCPs were thermally treated using the reaction sintering [8].

The apparent densities of the compacts were measured by the Archimedes principle in distilled water. The compacts were then heated at 4.3 K/min to 1100 °C. At certain temperatures, a compact was removed and analysed after cooling. Five samples prepared under the same conditions were analysed. The structural, compositional and impurity characteristics were studied by: X-ray powder diffraction (XRD, DRON-2, USSR diffractometer; CuK α radiation, 0.154 nm, step size 0.01°, counting time 1.5 s), combined thermogravimetry and differential thermal analysis (TG-DTA, Q-Derivatograph, Hungary, 5 K/min, air atmosphere), infrared spectrometry (IR, Spectrum One, Perkin-Elmer, USA; KBr-pellet technique) and dilatometry (TMV dilatometer, Ukraine). The crystal sizes in the powders were evaluated from the broadening of characteristic diffraction maxima using the Scherrer equation (in consideration of the instrumental broadening). The β -TCP/HA ratio was calculated from the integrated intensities of the main maxima of these phases [19]. The rel-

ative density ρ was obtained from the shrinkage curve values by the following equation:

$$\rho = \left[\frac{1}{1 - \frac{\Delta l}{l_0}} \right]^3 \cdot \rho_0 \quad (1)$$

where ρ_0 is the apparent density of the green compact at a heating temperature, and $\Delta l/l_0$ is the linear shrinkage assuming an isotropic process [19]. The Ca/P ratio was estimated by EDX spectroscopy (MAR-2, USSR) with an error of ± 0.01 .

III. Results and discussion

The XRD pattern of the uncalcined carbonated calcium phosphate (UCCP) sample at room temperature (RT) showed a mixture of an ACP and a nanocrystalline apatite (Fig. 1a). The nanocrystalline part unexpectedly became amorphous during the heating of UCCP to 300 °C because only a halo was present in the corresponding pattern. The XRD pattern of the sample heated at 500 °C (Fig. 1b), was the same, i.e. the amorphous state was preserved. The newly formed amorphous CP crystallized to an apatite phase with the HA structure at 700 °C (Fig. 1c). Beside apatite reflections, a weak peak at $2\theta = 31.05^\circ$ was present. Above 800 °C, the phase decomposed into HA and β -TCP. Beside maxima of these major phases, minor weak peaks can also be recognised (arrows in Fig. 1d,e). Because of their weak intensities and possible interactions, it is hard to identify the phase (or phases) that appeared. However, the peak at $2\theta = 31.05^\circ$ corresponds to β -TCP, because at 950 °C it transforms to the most intense (0210) reflection of this phase. The rest of the weak peaks could belong to impurities due to possible reactions of the formed pyrophosphates (see IR results further). In the XRD patterns of the UCCP heated to higher temperatures, no other phases were revealed, and the minor peaks gradually weakened up to 1100 °C (Fig. 1f).

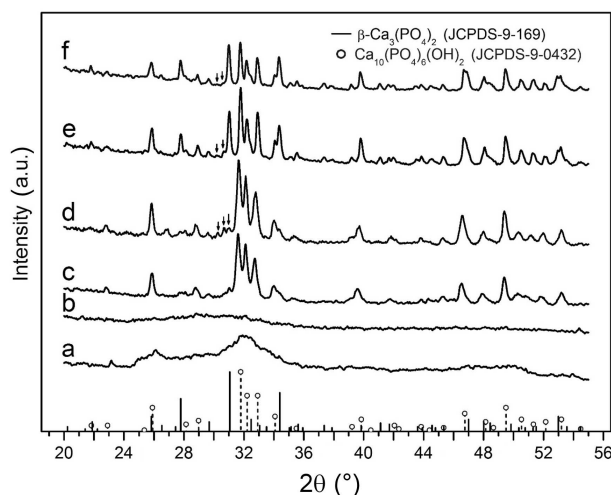


Figure 1. XRD patterns of UCCP at: a) 20 °C, b) 500 °C, c) 700 °C, d) 800 °C, e) 950 °C and f) 1100 °C

In the TG-DTA examination, the TG curve (Fig. 2a) of the heated UCCP revealed a continuous mass loss of about 25.7% up to 1000 °C. This curve was rather smooth and showed a mass loss of about 23.1% by the onset of crystallization (580 °C), 1.7% in the crystallization area (580–750 °C), and 0.9% in the range of 750–1000 °C. The accompanied DTA curve has a deep endominimum and a few poorly resolved superimposed endominima between RT and 400 °C, as well as two divided and extended exomaxima between 580–750 °C (ACP crystallization) and 750–970 °C (phase transformations) (Fig. 2). Similar TG/DTA curves are known for wet-synthesized and subsequently hydrolysed CP powder [16].

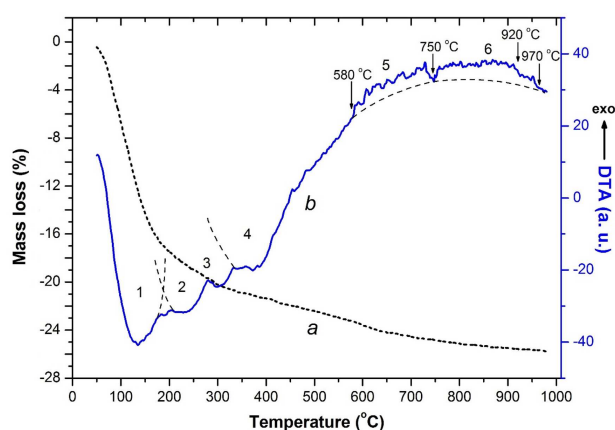


Figure 2. TG-DTA curves of the UCCP

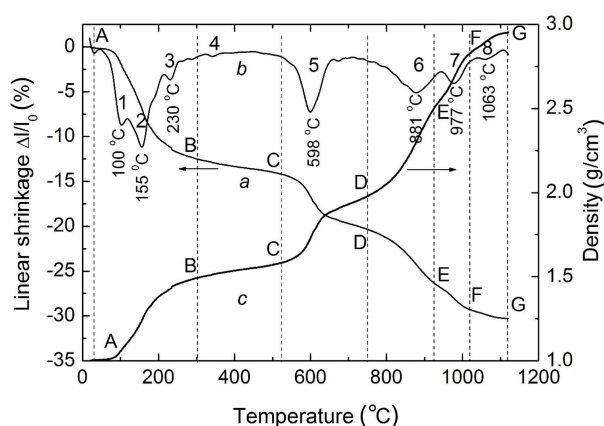


Figure 3. Linear shrinkage (a), linear shrinkage derivative (b) and apparent density (c) curves of the UCCP

The characteristics of the densification process turned out to be much more sensitive and informative compared to the TG-DTA changes in the UCCP (Fig. 3). The total linear shrinkage up to 1100 °C was 30.2% (curve a). The shrinkage resulted from the processes occurring in the following temperature ranges: AB, BC, CD, DE, EF and FG. In the AB range, the shrinkage was 12.5%, and three peaks 1–3 in the shrinkage rate curve (SRC) b were found. It is highly probable that the peaks were associated with the known thermal processes intensified

at the same (peak) temperatures in the wet-synthesized (hydrolysed) CP powders. They correspond to desorption of adsorbed (peak 1) and occluded (peak 2) water from the CP particles and exit of volatile gases (peak 3) due to the decomposition of the residual synthesis by-product NH_4NO_3 [16].

The IR spectra of the UCCP at RT and 300 °C confirm this assumption well. For the as-prepared UCCP, the IR spectrum shows very strong absorbance bands of adsorbed water at about 3398 cm^{-1} and 1649 cm^{-1} (Fig. 4a). Besides a strong PO_4^{3-} band at 1035 cm^{-1} and a weak one at 470 cm^{-1} , two PO_4^{3-} bands are present at 563 and 603 cm^{-1} . Because the last two are well separated, this means that beside an amorphous component (the non-split band at 1035 cm^{-1}), an apatite CP was also present in accordance with the XRD pattern (Fig. 1a). Strong CO_3^{2-} bands are present in the $1420\text{--}1490\text{ cm}^{-1}$ range. Taking also into account the distinct band at 873 cm^{-1} and the shoulder at 1510 cm^{-1} , it can be concluded that the nanocrystalline part of the UCCP was an AB-carbonated apatite phase with predominant B-type carbonation. The comparative analysis of the IR spectrum of the UCCP heated at 300 °C revealed that the water absorbance bands became considerably less intense, and the band at 3398 cm^{-1} was visibly narrower on the side of lower wave numbers at $3000\text{--}3250\text{ cm}^{-1}$ (Fig. 4b). This is because in this range the NH_4^+ absorptions are located [20], and the associated by-product was removed by heating (peak 3 in the SRC). The CO_3^{2-} bands also changed. The B-type absorbance bands became much weaker compared to the distinct A-type absorptions at 1434 and 1507 cm^{-1} . All PO_4^{3-} bands became unresolved and moved to 1047 cm^{-1} and 562 cm^{-1} proving that a completely amorphous carbonated CP was formed in accordance with the XRD data. These results showed that the shrinkage peaks 1–3 in the AB range were really caused by the water desorption, the decomposition products of the residual by-product, and, additionally, of some CO_2 from partly decomposed CO_3^{2-} ions. The last mentioned transformation proba-

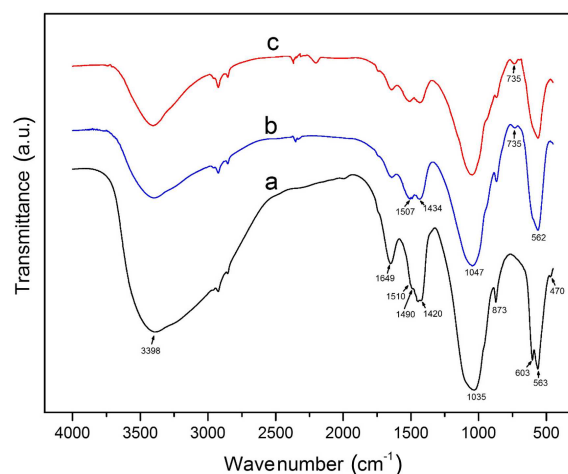
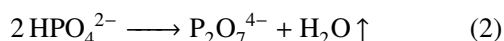


Figure 4. IR spectra of the UCCP at: a) 20 °C, b) 300 °C and c) 500 °C

bly caused the transformation of the apatite part into an additional ACP giving in the whole a carbonated amorphous UCCP at 300 °C.

The shrinkage in the BC range was small (1.7%) with a very small hypothetical peak 4 in the SRC at about 340 °C. According to the IR spectrum of the UCCP at 500 °C (Fig. 4c) it can be concluded that in this temperature range heating was accompanied with desorption of some water (the main band became narrower, its area decreased, and moved to 3405 cm⁻¹) and CO₂ (the CO₃²⁻ bands also somewhat decreased but their localization did not change). Additionally, the weak band in the spectrum recorded at 300 °C at 735 cm⁻¹ became somewhat stronger. This band is attributed to β -calcium pyrophosphate, Ca₂P₂O₇ (β -CPP) [21]. Consequently, despite the effective substitution of CO₃²⁻ for HPO₄²⁻ in the particles, the primary powder during their hydrolysis into the carbonated CP retained a little part in the previous state as amorphous CaHPO₄ (monetite; Ca/P = 1:1). Thus, the little shrinkage in the BC range was caused by a few but weak processes of the desorption of water and CO₂ from the decomposition of residual HPO₄²⁻ by the following reaction:



This reaction in the crystalline monetite intensifies at about 450 °C [21]. However, the decomposition temperature decreases to about 350 °C for an amorphous monetite [22]. Therefore, weak peak 4 could be real. The mass loss in the BC range was though much less than in the AB one (2.6% against 20.6%), but still measurable precisely.

The shrinkage rate peak 5 (Fig. 3) in the CD range was distinct, intense and its origin is clear because the UCCP crystallization occurred in this range (Fig. 1c). The mass loss here was still smaller than in the former one (1.5% against 2.6%), however, the shrinkage rate was much higher. To understand this seeming discrepancy, it is essential to take into consideration that the shrinkage and the densification in a sintering compact are directly connected [4,23]. The UCCP was prepared by using a hydrolysed powder dried by freezing at 5 °C. Although the obtained powder was well processable, it contained a great amount of the processing admixtures (in particular, about 23 wt.% of its total mass as shown by the combined mass loss in the AB and BC ranges, Figs. 2 and 3). To diminish the effect of such admixtures, an initial powder before compaction is usually preliminary calcined, or rather peculiar and complicated pressing techniques are used [4,23].

As the main idea of this study was to get suitable results by easy processing, the initial powder was used for compaction at a conventional pressure (100 MPa). All this resulted in an anomalous low apparent density in the UCCP of about 1.0 g/cm³ (Fig. 3c). However, the removal of the admixtures during heating in the AB and BC ranges resulted in the gradual densification of the

UCCP proportional to the lost masses. Therefore, the densification increase at the end of the AB range (at 300 °C) was substantially higher compared to that for the BC range (at about 550 °C). Because the majority of the admixtures was removed up to the onset of crystallization (only 1.5% mass loss was in the CD range), the intensive shrinkage (peak 5) and the corresponding enhancement in the density resulted from the structural changes in the UCCP. The occurred processes gave a perspective result: a compacted CP powder (UCCP) crystallized into a compacted apatite phase with a relatively high density of 1.98 g/cm³ (i.e. increased about twice compared to the “green” UCCP value) and was promising for further sintering.

The sintering up to 1100 °C of the crystallized UCCP was associated with three maxima 6, 7 and 8 (Fig. 3). The first two were rather intense, and the last one was weak. The origin of maximum 6 is explained by the XRD pattern of the UCCP heated at 950 °C (the minimum between peaks 6 and 7 in the DSC). The maxima in the XRD pattern of the sample heated at 800 °C were similar and somewhat more intense compared to those heated at 700 °C. The pattern of the sample sintered at 950 °C revealed a biphasic mixture of HA and β -TCP with somewhat decreased minor peaks (beside the intensified β -TCP peak at $2\theta = 31.05^\circ$, Figs. 1c-e). Consequently, the previously amorphous UCCP crystallized into a CDHA which decomposed into a BCP with the highest rate at about 880 °C (maximum 6). The XRD pattern of the formed BCP heated at 1030 °C showed that the ratio of intensity maxima of β -TCP/HA somewhat increased and the rest of minor impurity peaks further decreased compared to those in the former pattern. Hence, maximum 7 was associated with these changes. The similar but weaker tendency was revealed in the pattern of the UCCP heated at 1100 °C (Fig. 1f), indicating the same origin of maximum 8 (Fig. 3).

The IR spectra confirmed the XRD data well and gave additional information. The spectrum of the UCCP heated at 700 °C (Fig. 5a) showed bands of PO₄³⁻ ions at 1040 and 1087 cm⁻¹ (ν_3) and at 570 and 605 cm⁻¹ (ν_4). Beside them, a well-developed group of CO₃²⁻ bands was present at 1417, 1463, 1548 cm⁻¹ (ν_3) and 878 cm⁻¹ (ν_2). From this we deduced that the crystallized product was an AB-type carbonated apatite [24]. The middle band at 3405 cm⁻¹ and the associated weak bands at 3571 cm⁻¹ (OH⁻ stretching mode) and at 1641 cm⁻¹ reflected some adsorbed water. The spectrum of the crystallized UCCP heated at 800 °C was also informative (Fig. 5b). It contained the same PO₄³⁻ bands at 1038, 1088, 570 and 603 cm⁻¹, however, a weak peak at 725 cm⁻¹ and a shoulder at 756 cm⁻¹ were also present. The last two confirmed the presence of some residual HPO₄²⁻ ions in the UCCP after the hydrolysis which decomposed during heating according to reaction given in Eq. 2.

The reaction (Eq. 2) started at a moderate temperature when the UCCP was still amorphous because the shoul-

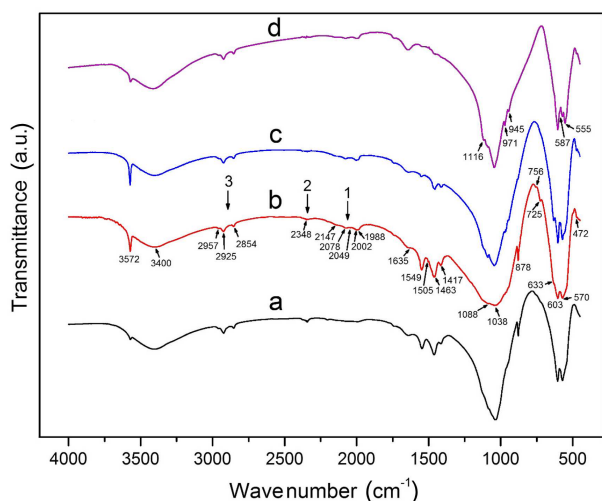
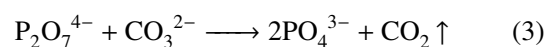


Figure 5. IR spectra of the crystallized UCCP at: a) 700 °C, b) 800 °C, c) 950 °C and d) 1100 °C

der at 756 cm^{-1} belongs to the metastable α -calcium pyrophosphate, $\text{Ca}_2\text{P}_2\text{O}_7$ (α -CPP), which transforms to the stable β -CPP polymorph at higher temperatures (indicated by the weak peak at 725 cm^{-1}) [16]. From this also follows that the assumed origin of the shrinkage peak 3 (Fig. 3) as a result of the given reaction was correct. The AB-CO_3^{2-} bands were present at the same wave numbers at 1417, 1463, 1549 and 878 cm^{-1} . They became stronger, and an additional band of this group appeared as shoulder at 1505 cm^{-1} [24]. The intensities of the water absorptions at 3400 and 1635 cm^{-1} slightly changed, however, the OH^- band at 3572 cm^{-1} was considerably stronger which can be associated with the appearance of a shoulder of the OH^- vibrational mode in the apatite at 633 cm^{-1} . The additional important feature was that the PO_4^{3-} bands became not only more intense but also much broader. All this means that the crystallization of the heated amorphous UCCP continued above 700 °C up to about 750 °C in full accordance with the first prolonged exomaximum in the DTA curve (Fig. 2).

The IR spectrum of the UCCP heated at 950 °C (Fig. 5c) substantially differed from that of the sample heated at 800 °C. Besides a weak peak at 474 cm^{-1} and well resolved bands at 572, 603, 632, 963, 1045 and 1090 cm^{-1} of HA, rather weak peaks and shoulders at 558(550), 945(945), 973(972) and 1124(1119) cm^{-1} of β -TCP appeared (the established β -TCP bands from the literature are given in parentheses [25]). The ν_3 and ν_4 bands of PO_4^{3-} became narrower. The AB-CO_3^{2-} absorbance bands at 1414, 1456, 1469, 1503, 1515 and 1563 cm^{-1} were present as weak peaks or hardly discernable shoulders. The water absorbance at 3405 cm^{-1} slightly decreased but the OH^- band at 3574 cm^{-1} significantly intensified. The last seems to be associated with the increased intensity of the OH^- band at 632 cm^{-1} . Instead of the CPP absorptions, only a hardly discernable shoulder at about 740 cm^{-1} was left. The removal of the $\text{P}_2\text{O}_7^{4-}$ ions from a CP can occur due to their reaction with OH^- or CO_3^{2-} [26,27]. In the spectra of the crys-

tallized UCCP heated up to 950 °C, the intensities of the OH^- bands became stronger, and those of CO_3^{2-} decreased, particularly of the A-type part. Consequently, the removal reaction was [27]:



It can result in less defective anionic groups and approaching of the formed HA to the stoichiometric composition. However, because of the low concentration of the $\text{P}_2\text{O}_7^{4-}$ ions, this process was weak and had only an auxiliary effect. Compared to the former data, the relative amount of β -TCP in the BCP increased after heating at 1030 °C (the spectrum is not shown here). The HA absorptions at 474, 572, 603, 631, 1045 and 1088 cm^{-1} became weaker and those of β -TCP at 555, 587, 945, 971 and 1116 cm^{-1} were noticeably stronger. The remaining AB-CO_3^{2-} absorptions at 1412, 1457 and 1548 cm^{-1} further decreased. The water bands at 3410 and 1644 cm^{-1} are slightly changed. The OH^- absorption at 631 cm^{-1} transformed to a very weak peak, and the OH^- band at 3572 cm^{-1} also decreased. The ν_3 and ν_4 PO_4^{3-} bands became narrower. These changes together with the XRD data indicated that a part of the residual HA transformed into β -TCP in the BCP giving in the EF range shrinkage rate maximum 7 ((Fig. 3, a densification) in the DSC curve. The spectrum of sample heated at 1100 °C reflects the continuation of the former tendency (Fig. 5d). The β -TCP bands became still more distinct and intense compared to those of HA. The most of CO_3^{2-} bands disappeared, the rest transformed to shoulders at 1457, 1491, 1503 and 1544 cm^{-1} . The water absorbance bands at 3414 and 1642 cm^{-1} are slightly changed. The OH^- band at 631 cm^{-1} disappeared and that at 3640 cm^{-1} became smaller.

Besides the absorbance bands given above, three groups of them were present in all spectra. They are most distinct in the spectrum of sample heated at 800 °C and labelled there with arrows (Fig. 5b). The first group is in the range of 1980–2150 cm^{-1} . The bands at 1988(1987), 2002(2003), 2049(2048), 2078(2078) and 2147(2145) cm^{-1} were assigned to either overtones or combinations (the established values for them are in parentheses) [28]. The weak bands around 2348 cm^{-1} are due to the surface-adsorbed CO_2 [27]. Finally, the bands at 2854, 2925 and 2957 cm^{-1} of the third group appeared due to the adsorbed hydrocarbon contamination [29].

Additional data on the phase and composition changes in the crystallized UCCPs came from the lattice constants. For the formed β -TCP phase, they showed the standard values of JCPDS card No. 9-169 within the experimental error of ± 0.0005 nm. However, the a constant of the CDHA was markedly changed (Fig. 6). It was 9.48 Å compared to the accepted value of 9.418 Å of stoichiometric HA (JCPDS card No. 9-432). This difference was caused by the dominant A-type CO_3^{2-} substitution in the AB-type carbonated HA (CDHA) because the B-type CO_3^{2-} substitution results in a

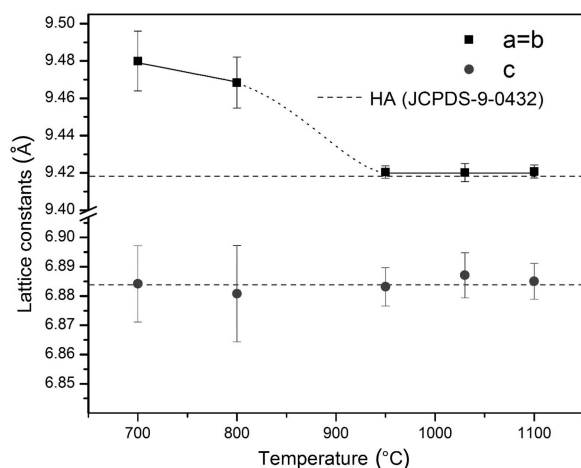


Figure 6. Changes in the lattice constants of the crystallized UCCP during heating at 700–1100 °C

decreased a constant [30]. According to the IR spectrum (Fig. 5b), heating of crystallized UCCP (CDHA) up to 800 °C led to an additional amount of crystallized material, but some CO_3^{2-} ions were simultaneously lost. As shown above, in the spectra of samples at higher temperatures, the A-type bands mostly decreased. It was also noted above that the water bands were weakly associated with the heating temperature of the crystallized UCCPs. Most probably, the water adsorbed into the pores of the UCCPs after their heating (during cooling) because the compacts were not fully sintered, especially at medium temperatures. Consequently, the mass loss of about 1.6% obtained by the TG measurement within 700–1100 °C was mainly caused by the CO_3^{2-} removal, and thus, the small a decrease up to 800 °C was really caused by the partial loss of the A-type CO_3^{2-} . The rapid decrease of the a constant to its standard value of the stoichiometric HA is also understandable. It was indicated above that the CO_3^{2-} bands were weak in the spectrum of sample heated at 950 °C. Although they became progressively weaker in the spectra at higher temperatures, the measurement accuracy of standard XRD analysis was not sufficient to reveal these minor changes in the BCP (UCCP) composition from the a constant decrease (as well as the known slight c constant changes in such cases [26]) up to 1100 °C compared to the high spectral sensitivity. All the main changes occurring in the UCCP within 750–975 °C were exothermic (Fig. 2b).

The densification step in the DE range (Fig. 3) was comparable with that in the AB range, however, it resulted from another mechanism. The heated BCP (UCCP) densified in the DE range due to two processes. The first was associated with the decomposition of the UCCP. By the XRD estimation, the formed BCP had a β -TCP/HA ratio of 40/60 giving a higher density of 3.12 g/cm³ compared to the density of 3.04 g/cm³ of the CDHA (UCCP) as determined from the lattice constants of the CDHA (UCCP) before its decomposition at 800 °C (Fig. 6). The ratio increased to 46/54 at 1030 °C

and only to 48/52 at 1100 °C indicating the depletion of the residual pristine CDHA. This resulted in lowering maxima 7 and 8 from the EF to the FG ranges (Fig. 3). Secondly, the wet-chemically synthesized CP particles heated to medium temperatures became connected by necks formed due to the surface diffusion giving slight densification of the heated body. At temperatures above 800 °C, the grain boundary diffusion is intensified, and some densification can occur. The increasing densification became dependent on the diffusion processes (additionally, the volume diffusion is joined at higher temperatures) [23], and because the reaction sintering exhausts, it can continue by ordinary sintering. Finally, the obtained BCP should be fired for some time at a desired temperature. The good results for such obtained BCPs can be predicted because the “initial” BCP at 1100 °C was already densified up to about 94% of its theoretical density (Fig. 3).

IV. Conclusions

Based on the assumption that some of the earlier observed reactions in a compacted wet-chemically synthesized calcium phosphate during heating might assist in its densification, thermal reactions in a compacted hydrolysed (in carbonated water) calcium phosphate powder were studied. Thus, uncalcined carbonated calcium phosphate (UCCP) compacts were prepared and densified by reaction sintering aimed to produce a suitable biphasic calcium phosphate composite with a ratio of hydroxyapatite/ β -tricalcium phosphate (HA/ β -TCP) of 48/52.

During heating in air, a number of reactions occurred in the UCCP. They were mainly the desorption of adsorbed water and gaseous components of a decomposed by-product between RT and 300 °C followed by the desorption of structural water and water from the condensation of the remnant HPO_4^{2-} ions between 300 and 530 °C. The crystallization of the amorphous UCCP occurs between 580 and 750 °C and the decomposition of the crystallized carbonated CDHA (calcium-deficient hydroxyapatite) to HA and β -TCP happens between 800 and 950 °C. Finally, the transformation of some residual CDHA into HA and β -TCP appears between 950 and 1100 °C. The CO_2 desorption due to the CO_3^{2-} decomposition is present in the medium temperature range. All the reactions made a different contribution to the observed densification of the UCCP, resulting in a significant densification of about 94 %TD of the finally formed HA/ β -TCP ceramics with the 48/52 ratio at 1100 °C. The results are reassuring because they shed a light on the insufficiently studied possibilities of using reaction sintering for a calcium phosphate densification and the most effective reactions in this process.

References

1. R.Z. Legeros, S. Lin, R. Rohanizadeh, D. Mijares, J.P. Legeros, “Biphasic calcium phosphate bioceramics:

- preparation, properties and applications”, *J. Mater. Sci.*, **14** (2003) 201–209.
2. J.M. Bouler, P. Pilet, O. Gauthier, E. Verron, “Biphasic calcium phosphate ceramics for bone reconstruction: A review of biological response”, *Acta Biomater.*, **53** (2017) 1–12.
 3. M. Bohner, B.L.-G. Santoni, N. Döbelin, “ β -tricalcium phosphate for bone substitution: Synthesis and properties”, *Acta Biomater.*, **2020**, **113** (2020) 23–41.
 4. S.V. Dorozhkin, “Multiphasic calcium orthophosphate (CaPO_4) bioceramics and their biomedical applications”, *Ceram. Int.*, **42** (2016) 6529–6554.
 5. X. Wang, H. Fan, Y. Xiao, X. Zhang, “Fabrication and characterization of porous hydroxyapatite/ β -tricalcium phosphate ceramics by microwave sintering”, *Mater. Lett.*, **60** (2006) 455–458.
 6. P. Sikder, Y. Ren, S.B. Bhaduri, “Microwave processing of calcium phosphate and magnesium phosphate based orthopedic bioceramics: A state-of-the-art review”, *Acta Biomater.*, **111** (2020) 29–53.
 7. C. Drouet, C. Largeot, G. Raimbeaux, C. Estournes, G. Dechambre, C. Combes, C. Rey, “Bioceramics: spark plasma sintering (SPS) of calcium phosphates”, *Adv. Sci. Technol.*, **49** (2006) 45–50.
 8. K. Ioku, T. Murakami, Y. Ikuma, M. Yoshimura, “Preparation of microstructure-controlled porous hydroxyapatite- β -tricalcium phosphate composites by reaction sintering”, *J. Ceram. Soc. Jpn.*, **100** (1992) 1015–1019.
 9. R. Famery, N. Richard, P. Boch, “Preparation of α - and β -tricalcium phosphate ceramics, with and without magnesium addition”, *Ceram. Int.*, **20** (1994) 327–336.
 10. K.C.B. Yeong, J. Wang, S.C. Ng, “Fabricating densified hydroxyapatite ceramics from a precipitated precursor”, *Mater. Lett.*, **38** (1999) 208–213.
 11. N. Jinlong, Z. Zhenxi, J. Dazong, “Investigation of phase evolution during the thermochemical synthesis of tricalcium phosphate”, *J. Mater. Synth. Proc.*, **9** (2001) 235–240.
 12. K. Yoshida, M. Kobayashi, H. Hyuga, N. Kondo, H. Kita, K. Hashimoto, Y. Toda, “Reaction sintering of β -tricalcium phosphates and their mechanical properties”, *J. Eur. Cer. Soc.*, **27** (2007) 3215–3220.
 13. S. Markovic, M.J. Lukic, S.D. Skapin, B. Stojanovic, D. Uskokovic, “Designing, fabrication and characterization of nanostructured functionally graded HAp/BCP ceramics”, *Ceram. Int.*, **41** (2015) 2654–2667.
 14. E. Hayek, W. Stadlmann, “Preparation of pure hydroxyapatite for adsorption use”, *Angew. Chem. Int. Ed.*, **67** (1955) 327–338.
 15. Z.Z. Zyman, D.V. Rokhmistrov, V.I. Glushko, “Structural and compositional features of amorphous calcium phosphate at the early stage of precipitation”, *J. Mater. Sci. Mater. Med.*, **21** (2010) 123–130.
 16. Z. Zyman, A. Goncharenko, O. Khavroniuk, D. Rokhmistrov, “Crystallization of metastable and stable phases from hydrolyzed by rinsing precipitated amorphous calcium phosphates with a given Ca/P ratio of 1:1”, *J. Cryst. Growth*, **535** (2020) 125547.
 17. F. Apfelbaum, I. Mayer, J.D.B. Featherstone, “The role of HPO_4^{2-} and CO_3^{2-} ions in the transformation of synthetic apatites to β - $\text{Ca}_3(\text{PO}_4)_2$ ”, *J. Inorg. Biochem.*, **38** (1990) 1–8.
 18. J.M. Toth, W.M. Hirthe, W.G. Hubbard, W.A. Brantley, K.L. Lynch, “Determination of the ratio of HA/TCP mixtures by X-ray diffraction”, *J. Appl. Biomater.*, **2** (1991) 37–40.
 19. M. Lukic, Z. Stojanovic, S.D. Skapin, M. Macek-Krmanc, M. Mitric, S. Markovic, D. Uskokovic, “Dense fine-grained biphasic calcium phosphate (BCP) bioceramics designed by two-step sintering”, *J. Eur. Ceram. Soc.*, **31** (2011) 19–27.
 20. Z. Zyman, M. Eppele, D. Rokhmistrov, V. Glushko, “On impurities and the internal structure in precipitates occurring during the precipitation of nanocrystalline calcium phosphate”. *Materwiss. Werkstofftech.*, **40** [4] (2009) 297–301.
 21. A. Gee, V.R. Deitz, “Pyrophosphate formation upon ignition of precipitated basic calcium phosphate”, *J. Am. Ceram. Soc.*, **77** (1955) 2961–2965.
 22. P. Layrolle, A. Lebugle, “Characterisation and reactivity of nanosized calcium phosphates prepared in anhydrous ethanol”, *Chem. Mater.*, **6** (1994) 1996–2004.
 23. E. Champion, “Sintering of CaP bioceramics”, *Acta Biomater.*, **9** (2013) 5855–5875.
 24. I.R. Gibson, W. Bonfield, “Novel synthesis and characterization of an AB-type carbonate-substituted hydroxyapatite”, *J. Biomed. Mater. Res.*, **59** (2002) 697–708.
 25. B.O. Fowler, E.C. Moreno, W.E. Brown, “Infra-red spectra of hydroxyapatite, octacalcium phosphate and pyrolysed octacalcium phosphate”, *Arch. Oral Biol.*, **11** (1966) 477–492.
 26. E.E. Berry, “The structure and composition of some calcium-deficient apatites. I and II”. *J. Inorg. Nucl. Chem.*, **29** (1967) 317–327.
 27. S.E.P. Dowker, J.C. Elliott, “Infrared study of trapped carbon dioxide in thermally treated apatites”, *J. Solid State Chem.*, **47** (1983) 164–173.
 28. B.O. Fowler, “Infrared studies of apatites. I. Vibrational assignments for calcium, strontium, and barium hydroxyapatites utilizing isotopic substitution”, *Inorg. Chem.*, **13** (1974) 194–214.
 29. T.S. Narasaraaju, D.E. Phebe, “Some physico-chemical aspects of hydroxyapatite”, *J. Mater. Sci.*, **31** (1996) 1–21.
 30. Z.Z. Zyman, D.V. Rokhmistrov, V.I. Glushko, I.G. Ivanov, “Thermal impurity reactions and structural changes in slightly carbonated hydroxyapatite”, *J. Mater. Sci. Mater. Med.*, **20** (2009) 1389–1399.