Carbonate substituted hydroxyapatite (CHA) powder consolidated at 450ºC

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Abstract. CHA powder was consolidated without noticeable changing of its carbonate content using low-melting Na-Ca phosphate glass with the composition referred to 54% Na₄CaP₆O₁₈ and 46% Na₂CaP₂O₇ as a binder. A temperature window suitable for obtaining the composite was assessed as 450 - 475ºC. The composites obtained at 450ºC and 400 MPa for 1 hr demonstrate compressive strength up to 25 MPa.

1. Introduction

Hydroxyapatite Ca₁₀(PO₄)₆(OH)₂ (HA) is widely used as clinically approved material for bone tissue replacement since its chemical composition is quite close to inorganic part of a human bone. HA implants are biocompatible, although the rate of their remodeling in vivo is too low to induce a massive formation of a new bone, and, thus, the HA implant serves as a substituent of the lost part of a bone. However, prominent trend in orthopedic and maxillofacial surgery is related to a regenerative approach which implies rather fast resorption of the implant material and simultaneous filling of respective resorption lacunas with newly formed bone. Pure HA has a limited potential in the frame of regenerative approach due to its low bioresorption rate [1]. Materials based on carbonate-substituted hydroxyapatite Ca₁₀₋ₓNaₓ(PO₄)₆₋ₓ(CO₃)ₓ(OH)₂ (CHA) are more prospective since their chemical composition approximates that of inorganic part of a bone tissue more accurately [2], and its rate of bioresortption is high enough [3] due to structural distortions occurring under carbonate anion incorporation into the crystal lattice.

Choosing CHA as a material for bone implants immediately requires special technique for its consolidation into bulk bodies. Conventional method of solid state sintering cannot be applied for the case of CHA since it starts to decompose at temperatures higher than 700ºC into pure (stoichiometric) HA and CaO with CO₂ release [4,5]. This problem can be overcome by selection of an appropriate binder with low melting point. Thereby, the process of consolidation can be described in terms of liquid-state sintering running essentially in liquid-state environment. Naturally, the binder has to be biocompatible, i.e. has to contain calcium, phosphorus and/or other biogenic elements. The next requirement is connected with binder melting point that should be reasonably low, less than the decomposition point of CHA, but high enough to provide the melt with low viscosity, otherwise molten binder cannot fill pores and capillary channels between CHA particles in a green body. From
these viewpoints, quasi-binary section Na₄CaP₆O₁₈ - Na₂CaP₂O₇ of CaO – Na₂O - P₂O₅ ternary system looks very attractive as one can find there eutectics (54% Na₄CaP₆O₁₈ and 46% Na₂CaP₂O₇) melted at 473°C [9]. Pyro- and polyphosphate species composing the eutectic facilitate supercooling of the melt and, thus, enable to quench the melt into glass which can be soften at temperature even lower than the melting point.

In the present paper, we report on the possibility to consolidate CHA powder without noticeable changing of its carbonate content using low-melting Na-Ca phosphate glass with the above composition as a binder.

2. Experimental

2.1. Preparation of CHA powder

CHA powder was prepared by precipitation from aqueous as described in [6-8] according to reaction (1). Chemically graded (NH₄)₂HPO₄, Ca(NO₃)₂·4H₂O, NaHCO₃ and 30 wt. % ammonia solution were used as raw materials.

\[
8.5\text{Ca(NO}_3\text{)}_2 + 4.5\text{(NH}_4\text{)}_2\text{HPO}_4 + 1.5\text{NaHCO}_3 + 8\text{NH}_4\text{OH} \rightarrow \\
\text{C}_8\text{b}_{\text{Na}_{1.5}}(\text{PO}_4)_{4.5}(\text{CO}_3)_{1.5}(\text{OH})_2 + 17\text{NH}_4\text{NO}_3 + 6\text{H}_2\text{O}, (1)
\]

Stoichiometric amount of NaHCO₃ was added to 0.3 M (NH₄)₂HPO₄ solution, and pH was adjusted to 11 ± 1 by adding ammonia. 0.5 M Ca(NO₃)₂ was added to the above solution drop wisely under vigorous stirring and temperature T=40°C. The CHA-precipitate was maturated for 24 hours in mother liquor followed by filtration at Buchner funnel. This precipitate was thoroughly washed with distilled water (more than 1 litter) to remove by-products, and, then, was dried at T=60°C for 24 hours. Thermal treatment at 260°C for 1 hour was applied for complete elimination of NH₄NO₃ by-product.

2.2. Fabrication of low-melting phosphate glass

Phosphate glass composed of 54% Na₄CaP₆O₁₈ and 46% Na₂CaP₂O₇ was obtained from CaHPO₄ (obtained by precipitation from Ca(NO₃)₂·4H₂O and (NH₄)₂HPO₄ solutions), NaH₂PO₄, Na₂HPO₄*12H₂O, Ca(H₂PO₄)₂ precursors according to reactions (2-7) followed by mixing Na₄CaP₆O₁₈ and 46% Na₂CaP₂O₇, subsequent melting at 950°C for 6 hours and quenching (by pouring the melt onto the cold steel plate).

\[
\text{2CaHPO}_4 \rightarrow \text{Ca}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} \uparrow \\
\text{NaH}_2\text{PO}_4 \rightarrow \text{NaPO}_3 + \text{H}_2\text{O} \uparrow \\
\text{2Na}_2\text{HPO}_4 \rightarrow \text{Na}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} \uparrow \\
\text{Ca(H}_2\text{PO}_4\text{)}_2 \rightarrow \text{Ca(PO}_3\text{)}_2 + 2\text{H}_2\text{O} \uparrow \\
\text{4NaPO}_3 + \text{Ca(PO}_3\text{)}_2 \rightarrow \text{Na}_4\text{CaP}_6\text{O}_{18} \\
\text{Na}_2\text{P}_2\text{O}_7 + \text{Ca}_2\text{P}_2\text{O}_7 \rightarrow 2\text{Na}_2\text{CaP}_2\text{O}_7
\]

2.3. Fabrication of CHA based composite materials

The CHA powders were mixed with 40 wt.% of the phosphate glass in a ball mill for 30 min under acetone (powder/balls ratio was set to 1:4). The resulted powder was dried at 100°C for 24 hours. Thus obtained mixture was annealed at 450, 500, 600 and 700°C (t=24 h) in order to choose consolidation temperature (heating rate was about 5°C/min, after annealing the samples were quenched to room temperature in air). Two different ways were used to consolidate the composites – “warm” pressing at T=250°C and P=450 MPa for 6 hours (Fig. 1a) and hot pressing at T=450°C and P=200 MPa for 3 hours (Fig. 1b).
3. Sample characterization

All samples were studied by X-ray diffraction analysis in the interval of angles $2\theta = 20–70^\circ$ (Cu Ka radiation, Rigaku D/MAX 2500 with rotating anode, Japan). The micromorphology of the samples was examined by scanning electron microscopy (LEO SUPRA 50VP, Carl Zeiss, Germany, 5 kV). The carbonate content was analyzed via microvolumetric determination of CO$_2$ released from the samples under their dissolution in nitric acid. The overall content of CO$_2$ and H$_2$O was examined by TG/DTA (Diamond Pyris, Perkin Elmer, USA, quasi-isothermal heating to maintain decomposition rate at 10 µg/min; STA 409 PC, Netzsch, Germany, with IR-analysis of evolved gases). Distribution of particle sizes in powders was quantified by dynamic light scattering method (Analysette-22, Fritsch, Germany) in a window of 0.2-100 µm with preliminary ultrasonication for 20 s.

Compressive strength of the cylindrical samples was determined in the test of their axial loading (crosshead rate 1 mm/min) using electromechanical universal machine Instron 5982 (Instron, UK, ultimate load up to 100 kN). Height/diameter ratio of the cylindrical samples was adjusted to 2:3; both bases of the cylinders were made parallel by polishing.

4. Results and discussion

Details of variation of CHA properties with carbonate content can be found elsewhere [4]. Briefly, an increase of carbonate content gives rise to a particle size decrease as well as to a microstrain increase (and, therefore, solubility enhancement). Coming from this point, CHA samples with maximal carbonate content are prospective in sense of fabrication of bioresorbable implants.

The sequence of transformations occurring in the phosphate glass binder under its heating can be deduced from DTA-curve (Fig. 2). It is apparent that transition in glass connected with its devitrifying and softening takes place at about $T \sim 450^\circ$C as it is evidenced by step-wise behavior of the DTA base line. Exothermal effect at $T \sim 550^\circ$C has to be attributed to crystallization of the glass, and prominent endothermic effect at $T \sim 750^\circ$C corresponds to global melting of the sample. It is of note that the last temperature points a maximum of the rate of melt formation, rather than the melt starting which seems to occur earlier, just after crystallization of the glass proceeds. Nevertheless, a contradiction on melting point of this composition between literature data and our experiment still exists. Feasible explanation of this fact can be made assuming that in our glassy samples melting is not an equilibrium process apart from [9], where attaining the equilibrium is a key factor to construct a phase diagram. However, it is quite clear that the temperature of composite processing should lie in the interval 450-700°C.
The mixture CHA/glass (60% mass. CHA and 40% mass glass) was sintered at different temperatures, namely 450, 500, 600 and 700°C and according to XRD, chemical interaction of CHA with the glass starts at temperature $T = 475 \pm 25°C$ (Fig. 3). This phenomenon narrows the interval suitable for the composite processing to 450-475°C.

Interestingly, XRD peaks of $\beta$-TCP ($Ca_3(PO_4)_2$) phase have considerable shift with respect to correspondent ICDD-data. Such an observation implies the fact of sodium incorporation into TCP lattice. Since $\beta$-TCP phase appears already at about 500°C, right in between devitrifying and crystallization, this temperature can be regarded as a starting one for CHA reaction with glass environment with the accuracy of a half of a temperature step in our annealing experiments (i.e. 25°C).

Our attempts to consolidate the mixture CHA/glass via conventional sintering at 450-500°C give no yield: thus “sintered” samples demonstrate rather weak strength (less than 5 MPa). It looks exactable since the main atomic mechanism of sintering glassy matrix is viscous or creep flow, the rate of which depends on matrix viscosity being the function of temperature. The driving force for sintering is either capillary or external pressure. Therefore, affective densification of the composite of CHA in a viscous thermoplastic matrix assumes elevated temperatures and pressures.
Another factor affecting consolidation is uniform distribution of CHA and glassy phases across the bulk of the samples. Apparently, that homogeneity of such distribution depends on proximity of particle sizes for both phases. Laser diffraction analysis showed that in the case of phosphate glass bimodal distribution with the modes of 11 $\mu$m corresponded to the average of primary particle aggregates, and of 44 $\mu$m - attributed by us to secondary aggregates. The cases of CHA and CHA/glass mixture look quite similar to the described above (Fig. 4). Although, the size of CHA crystals are less than 100 nm and, therefore, a large (10 $\mu$m in magnitude) particle of the glass is surrounded by a shell with comparable thickness composed of 100 nm particles of CHA.

According to SEM intrusion of CHA particles composing the shell into the glass particle takes place under “warm” pressing (Fig. 5). A viscosity of the glass is likely to be rather high under these conditions, and the glassy matrix cannot fill all pores and channels for the time less than 6 hrs. Extending the time of such procedure is hardly attractable from practical viewpoint.

![Particle size distribution in CHA, phosphate glass and CHA/glass mixture powders after milling.](image1)

**Fig. 4.** Particle size distribution in CHA, phosphate glass and CHA/glass mixture powders after milling.

![Microstructure of the sample obtained by “warm” pressing.](image2)

**Fig. 5.** Microstructure of the sample obtained by “warm” pressing.
Hot pressing at 450°C and pressure of 400 MPa leads to more effective creep of glass in comparison with the temperature of 250°C owing to considerable drop of glass viscosity behind the devitrifying region (Fig. 6). However, a decrease of viscosity is still not enough for effective densification in a time scale of 1 hour, since according to SEM data one can find some regions where CHA particles do not contact with the glass matrix. Perhaps, an increase of hot pressing time at temperature 450°C enables to obtain more homogeneous composite material with enhanced mechanical properties.

Thereby, formation of a composite material with phosphate glass as a matrix and CHA as a filler, combines two processes – intrusion of solid CHA particles into the glass matrix and a viscous flow of the glass into intergranular spaces by both capillary forces and external pressure. Since the creep rate of the glass is rather low, it needs definitive time for large glass particles to flow into the pores between CHA crystals (see Fig. 7).

![Fig. 6. Microstructures of the samples obtained by hot pressing.](image)

![Fig. 7. Scheme of formation of the composites under study during hot pressing.](image)

It is worth to note that according to chemical analysis both hot and “warm” PRESSED SAMPLES do not change significantly their carbonate content (Table 1); the content for both types of the samples as well as of starting CHA coincide within the accuracy of the analysis. This fact also supports that under chosen conditions neither interaction between CHA and glassy matrix occurs.

| Table 1. Carbonate content in the CHA powder and the composites after high temperature pressing. |
|---------------------------------------------------------------|
| CHA | CHA/glass (T=250°C) | CHAP/glass (T=450°C) |
| ω(CO₃²⁻), wt. % | 7.5 ± 0.3 | 7.2 ± 0.5 | 6.9 ± 0.5 |

The samples fabricated by hot pressing technique were machined to shape necessary for correct mechanical testing (Fig. 8) (height/diameter ratio 3:2). It was found that the composites are easily machinable (via cutting and grinding) compared to HA ceramics obtained by solid-phase sintering due to moderate strength values.
Fig. 8. The composite fabricated by hot pressing machined for compressive strength test.

Evidently, the samples obtained by hot pressing at 450°C had better compressive strength values – 25 MPa compared to “warm”-pressed samples – 6 MPa. There is no doubt that the reason underlying such a behavior consists in significant drop in viscosity of the glass matrix at 450°C that leads to more effective intergranular space filling and better adhesion of filler particles to the matrix.

5. Conclusions

We have demonstrated that there is a possibility to consolidate CHA powder without noticeable changing of its carbonate content using low-melting Na-Ca phosphate glass with the composition referred to 54% Na₄Ca₃P₆O₁₈ and 46% Na₂CaP₂O₇ as a binder. A temperature window suitable for obtaining the composite was assessed as 450 - 475°C since at 475±25°C the interaction between CHA and phosphate glass matrix starts. The main process contributing to overall densification of the samples is a viscous flow of the glass matrix under external pressure. The composites obtained at 450°C and 400 MPa for 1 hr demonstrate compressive strength up to 25 MPa.

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