

SINTERING OF POROUS CARBONATED APATITE BIO-CERAMICS

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Abstract

Experiments were performed relating to the synthesis, thermal decomposition and sintering of carbonated apatite, aiming at revealing routes of preparation of porous ceramics intended for medical applications as bone tissue substitute. A novel synthesis technique was developed allowing the preparation of the AB-type substituted apatite. Temperature dependences of the release of carbon monoxide and carbon dioxide from the carbonated apatite were studied by Fourier transformed IR spectroscopy of the condensed gas phase. It was shown that porous ceramics can be fabricated by sintering in an air atmosphere at temperature no higher than 1000°C. Small additives of sodium orthophosphate enhance the sintering densification, but induce considerable grain growth. Low melting temperature eutectics were ineffective as additives for sintering of carbonated apatite ceramics. Ceramics of about 35 vol.% pore content and 0.5-2.0 μm pore size were prepared with microstructures considered favourable for expected biological application of ceramics.

Keywords: biomaterials, ceramics, calcium phosphate, carbonated hydroxyapatite, sintering, thermal decomposition, FTIR

INTRODUCTION

Bioactive ceramic substrates capable of incorporation into the natural process of bone reconstruction are of great interest in surgical application. For this purpose, porous calcium phosphate ceramics were widely studied and have been already employed in practice [1-3]. These materials, usually composed of hydroxyapatite (HA, chemical composition $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) have recently been tested as scaffolds for bone tissue engineering - a biologically based method for the repair and regeneration of tissues, due to their biocompatibility and osteoconductive behavior. In the bone tissue engineering approach, osteogenic cells are harvested from the patient and seeded onto a synthetic scaffold, that acts as a guide and stimulus for tissue growth, creating a tissue engineering construct or living biocomposite. The biocomposite would then be implanted back into the patient [4]. An alternative approach is to attach to the scaffold the bone morphogenetic proteins which provide the construct for osteoinductivity [4]. In both the cases, the control of porosity, pore size, pore interconnectivity, and chemical behavior of the ceramics is needed [4].

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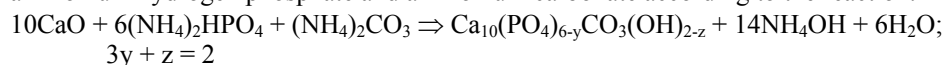
Carbonate substitutions in the HA structure are known to affect chemical properties. Human bone always consists of carbonated HA (CA), which is more soluble by the extracellular body fluids compared to HA [5]. The carbonate content in the bone mineral is about 3 to 8 wt.%, being dependent on the age of the individual [6]. The carbonate groups create lattice distortion, microstresses and crystal defects affecting *in vivo* behavior. Enhanced solubility increases a trend to induce precipitation of bone-like apatite, which effectively contributes to bone tissue formation [7]. For this reason, the development of a technology to fabricate porous CA ceramics seems to be an important matter.

The carbonate groups can competitively substitute at two sites in the apatite structure, namely the hydroxyl and the phosphate group positions, giving A- and B-type carbonated apatite, respectively [8]. These two types of substitution can occur simultaneously, resulting in a mixed AB-type substitution [9,10]. The apatite that constitutes bone mineral is considered to be always of AB-type, the share of the B-type substitution being predominant over the A-type [8]. When AB-type CA was heat-treated in an air atmosphere, phase decomposition occurred at temperature as low as 750°C [11]. The sintering temperature of HA ceramics exceeds 1000°C, being of about 1300°C to obtain a full, dense ceramic body [12]. Therefore, the sintering behavior of CA should be competitively influenced by its thermal decomposition and sintering densification processes. The thermal decomposition can be affected by the CA synthesis technique and route. Sintering additives could be employed to control the densification, i.e. through either a liquid phase or an intermediate compound formation during the sintering route. For example, a small addition of sodium phosphate has been revealed to enhance the densification rate and to decrease the sintering temperature of HA ceramics [13,14]. In this respect, the present study was aimed at the investigation of the thermal decomposition of the CA, prepared by a novel synthesis technique and its sintering with the use of some additives.

EXPERIMENTAL

Materials

The synthesis method consisted of the interaction between calcium oxide, ammonium hydrogen phosphate and ammonium carbonate according to the reaction:



Initial reagents (analytical grade) were mixed at equimolar ratios, according to the reaction above, in a planetary ball mill for 30 min. After that, H₂O was added to the mixture and the mixing was continued for 30 min. The mix was placed in a domestic microwave oven (Electronica, 2.45 GHz frequency, 630 W power) for 40 min, because the microwave treatment is known to accelerate the synthesis of carbonated apatite [15]. The reaction product, white powder, was then subjected to a heat treatment at 300°C in an air atmosphere furnace.

The reaction product, white power, has the following characteristics: X-ray density 3.12 g/cm³, BET specific area 2.53 m²/g, crystallooptic indexes $n_g = 1.651$ and $n_p = 1.644$, as measured using an immersion liquids set. Individual particles size was from about 0.5 to 2 μm, the particles being agglomerated into the granules of 10 to 25 μm size. To crush the agglomerates, those were subjected to milling in a planetary ball mill in an ethanol media, resulting in an increase of specific area up to 4.74 m²/g.

Both the individual alkali phosphate salt and the eutectic mixtures of salts were used as the sintering additives. The additives should contain no hazard ions. The

composition of the additives and their melting temperatures are given in Table 1. The additives were prepared in a planetary mill and added to the CA powder as a solution in ethanol. After drying at 80°C, the powders were plasticified by polyvinylbutiral and sieved with a sieve of 300 µm cell size.

Tab.1. Sintering additives.

Additive composition [wt.%]	Na ₃ PO ₄	Na ₃ PO ₄	25KPO ₃ – 5NaPO ₃	3NaPO ₃ – 97Na ₃ PO ₄
Melting temperature* [°C]	1340	1340	545	940
Amount added [wt.%]	2	5	5	5

* Ref. [16]

Green ceramic bodies were pressed into the discs of 10 mm diameter under a pressure of 100 MPa up to a pressing relative density of about 55 %. The samples were then sintered at a temperature of 1000°C in an air atmosphere furnace (the rate of heating up to 1000°C was 3°/min). Five batches were studied: CA (1), CA-5 % (25 % KPO₃ - 75 % NaPO₃) (2), CA-5 % (3 % NaPO₃ - 97 % Na₃PO₄) (3), CA-5 % Na₃PO₄ (4) and CA-2 % Na₃PO₄ (5).

Methods

Chemical analysis for carbon content was performed according to the Russian Standard GOST procedure employing the measurement of the volume of gas produced by the reaction between sample and hydrochloric acid [17].

Infrared (IR) spectra of both the initial powders and the residue after heat treatment, mixed with KBr, were recorded using a Bruker Equinox 55 Interferometer in diffuse reflectance mode with a resolution of 1 cm⁻¹ accumulating 200 scans.

The apparatus to perform the FTIR spectroscopic study of the gas phase released from the decomposing sample consists of a cooling system - cryotype (Displex, Air Products and Chemicals 202 CSA) located in a home made of the high vacuum stainless steel shroud – connected under rotary vacuum to a Bruker IFS 113v Interferometer through a suitable IR-transparent CsI window. Details of the apparatus have been described elsewhere [18]. The CA samples have been vaporized under equilibrium conditions from tantalum Knudsen cells having orifices of 1 mm in diameter. The vaporization temperature was increased by steps of 150°C in the range of 180-1600°C. Matrix gas (Ar) and evaporating species were condensed at T ≈ 12 K on the gold-plated cold finger. About 200 scans were accumulated with a resolution of 1 cm⁻¹. Blank spectra have been recorded with an empty cell holding all parameters similar to those used through the experiments with the samples.

X-ray diffraction (XRD) analysis was performed using a Philips X'Pert SW diffractometer (Cu K_α radiation λ = 1.54056 Å, scan type: continuous; scan step size 0.01671 deg; time per step: 2 s; number of counts: 5386). Lattice constants, *a* and *c*, were calculated by least squares refinements, using equations for a hexagonal cell (space group P6₃/m) given in [19].

Microstructural study was performed by scanning electron microscopy (SEM) observations using a LEO 1450 VP microscope. Open porosity was measured by an Archimedeian method of hydrostatic weighting of the samples in distilled water.

RESULTS AND DISCUSSION

According to chemical analysis, the carbon content in the samples was 1.56 ± 0.2 wt.%, being more than the predicted value of 1.17 wt.%. XRD patterns of the samples heat-treated at 300°C, and the exposed *in situ* within the diffractometer camera at 850, 900, 950 and 1100°C samples, respectively, are shown in Fig.1. The calculated lattice constant of initial CA were $a = 9.410(1)$ Å and $c = 6.884(1)$ Å, being close to the data reported for different carbonated hydroxyapatites [1]. The calcium carbonate peaks can clearly be observed at 2Theta 29.40 and 39.40 for the initial powder, and powders exposed at 850 and 900°C. The calcium carbonate content does not exceed approximately 3 wt.%, according to the estimation using an internal standard method (synthetic calcite R 50586 sample has been used as internal standard). After exposure to 950°C and above, a diffraction peak at 2Theta 37.50 appeared, resulting from CaO due to the partial phase decomposition of either the CA or the calcium carbonate [1,10]. Indirectly, the formation of CaO as the decomposition product indicates that the CA was of AB-type, having a Ca/P ratio greater than 1.67 [10]. In the opposite case of A-type CA, the decomposition products might be tricalcium phosphate and tetracalcium phosphate [20]. Generally, XRD pattern of CA at 1100°C retained all features of HA-like structure. The peaks from calcium carbonate disappeared at 900°C and above, probably due to the decomposition occurring at this temperature [21].

Figure 2 shows FTIR spectra of the initial powder, and the residue after the heat-treatment at 1100°C. Hydroxyl groups stretch mode near 3570 cm^{-1} disappeared after heat treatment at 1100°C. Peaks in the region of 1650 to 1300 cm^{-1} are due to ν_3 vibrational mode carbonate ion, and the peak at 873 cm^{-1} is due to the carbonate ν_2 vibrational mode [20,22]. The ratio of ν_3 carbonate band area to ν_3 phosphate band area is known and can be used as a measure of carbonate/phosphate ions ratio [20]. It can be concluded from the spectra given in Fig.2 and the XRD data that the CA sample still retains some amount of carbonate groups after being exposed to 1100°C, however, the carbonate loss may be significant.

Figure 3 shows CO and CO₂ bands in the spectra of the gaseous phase released during the heating of the CA sample in a wide temperature range, starting from 300°C. Both oxides were surely originated from the samples, in view of their negligible intensity in the blank spectra at respective vaporization temperature. Carbon monoxide absorbs at 2148.9 and 2138.2 cm^{-1} with a shoulder at 2142.5 cm^{-1} , while the bands at 2344.8 and 2339.4 cm^{-1} are assigned to the asymmetric stretching mode of CO₂. The calculated area, which could be considered as a measure of content of the CO and CO₂ bands *versus* vaporization temperature is shown in Fig.4. It becomes clear that CO evolution starts at about 500°C and goes through a maximum at about 1000°C. The trend in the CO₂ peak area *versus* vaporization temperature differs from that revealed for the CO band, evidencing a maximum in the temperature range from 500 to 800°C followed by rapid decrease in CO₂ evolution, probably due to the decomposition of carbon dioxide into monoxide and oxygen in the gas phase. The data indicate a significant carbonate release at 1000°C and above. Thus, the sintering temperature of CA ceramics should be limited at 1000°C, not higher, to retain the ceramics composition at least close to the predicted level.

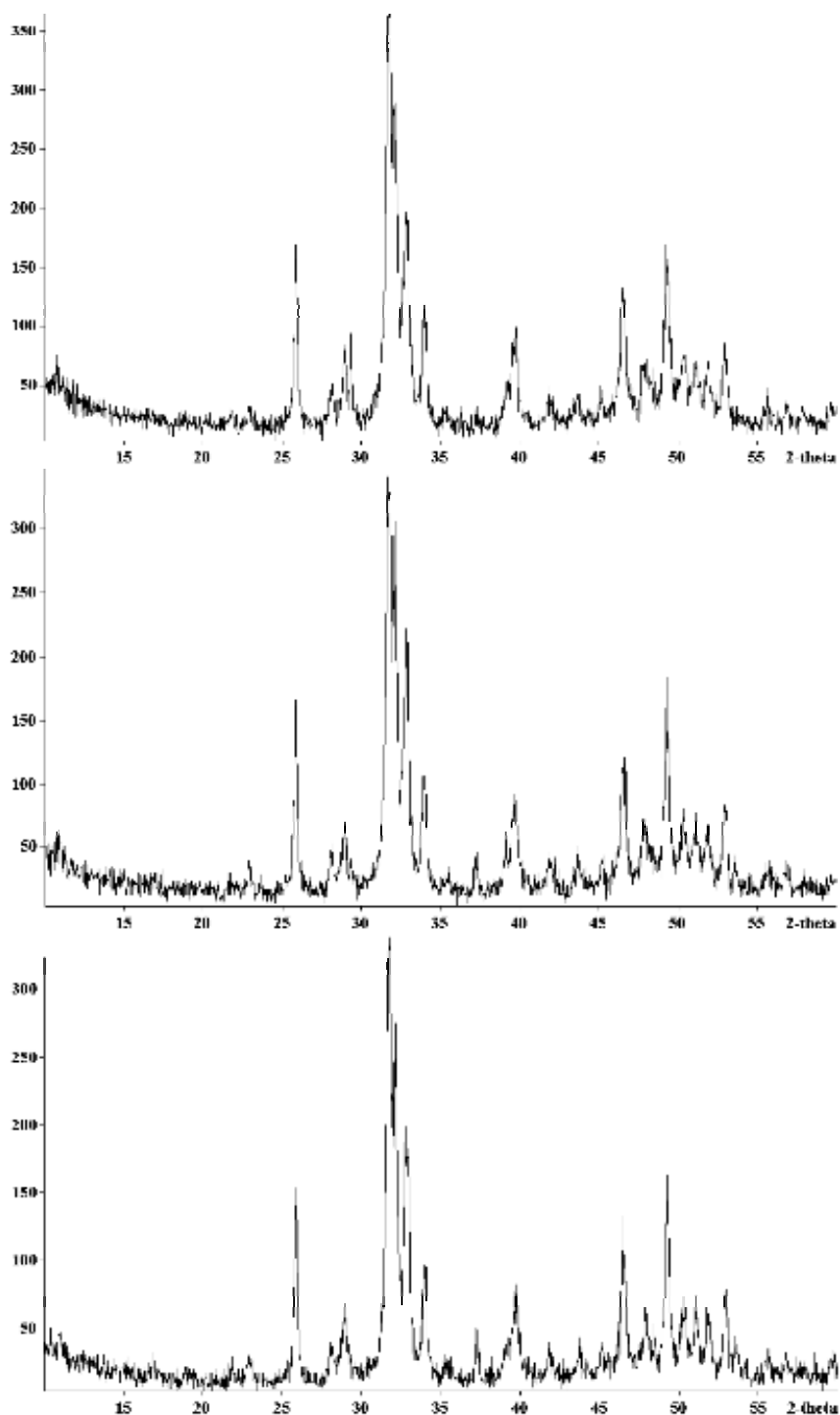


Fig.1. XRD patterns of CA powder at 850°C, 950°C and 1100°C. • - calcium carbonate; ■ - calcium oxide.

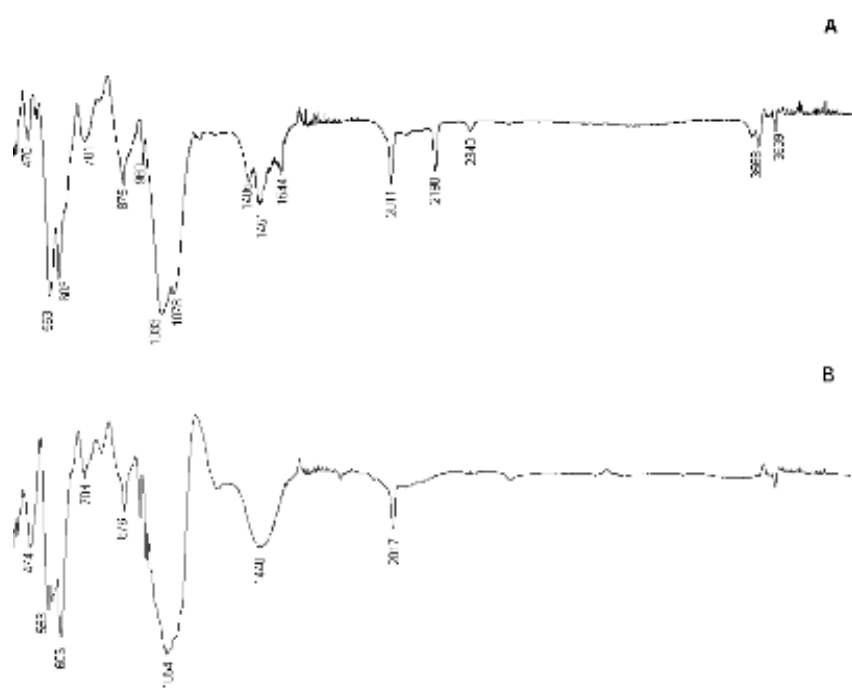


Fig.2. FTIR spectra of initial CA powder (a) and residues after exposure to 1100°C (b).

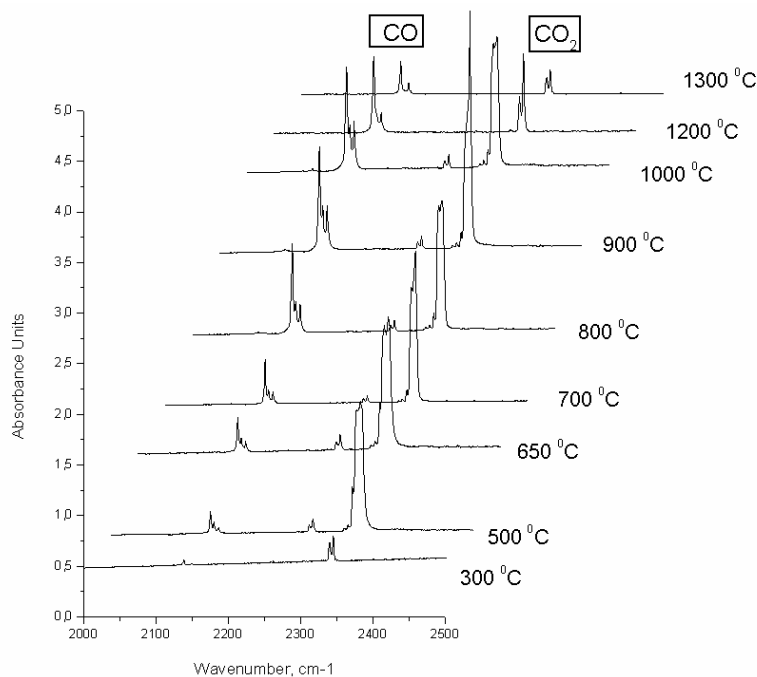


Fig.3. CO and CO₂ bands in FTIR spectra of gaseous phase released from CA in the wide temperature range.

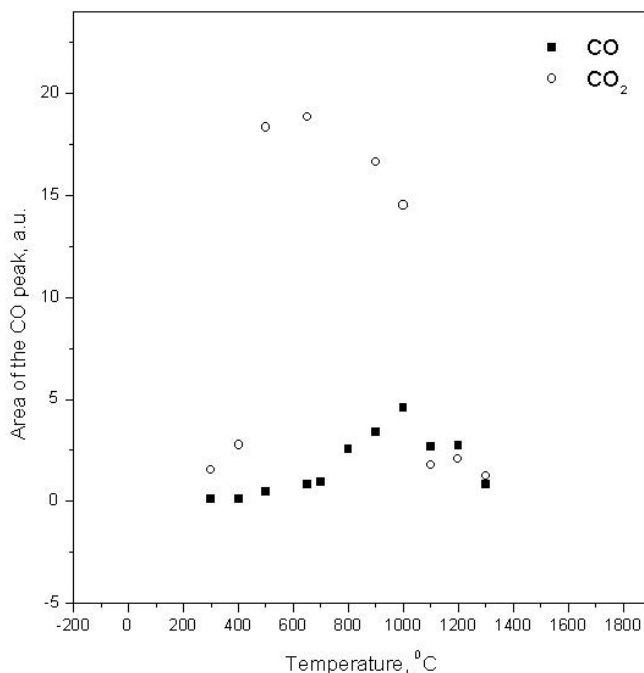


Fig.4. Area of CO and CO₂ peaks *versus* vaporization temperature.

Shown in Figure 5 are the shrinkage and open pores content in CA ceramics sintered without, and with, the additives. At equal sintering conditions, an addition of sodium orthophosphate allows one to reduce somewhat the porosity of ceramics from 48.8 % down to 34.7 %, whereas low melting eutectic additives, forming a liquid at sintering temperature, were not effective. Sodium orthophosphate is known to form at high temperature an intermediate compound, β -NaCaPO₄, when added to HA, enhancing the sintering densification [13,14]. Figure 6 shows SEM micrographs of sintered CA and CA-5 wt.% Na₃PO₄ ceramics. The additive can be seen to induce the grain growth significantly, somewhat enlarging the pore size. The Image J analysis programme was applied to evaluate the mean pore size. It equals 0.47 μ m for CA ceramics, and 0.54 μ m for CA-5 % Na₃PO₄ ceramics. The pore size at the level of submicrometers seems to be favourable to the adsorption of proteins to the ceramics, improving their biological behavior as bone tissue substitute.

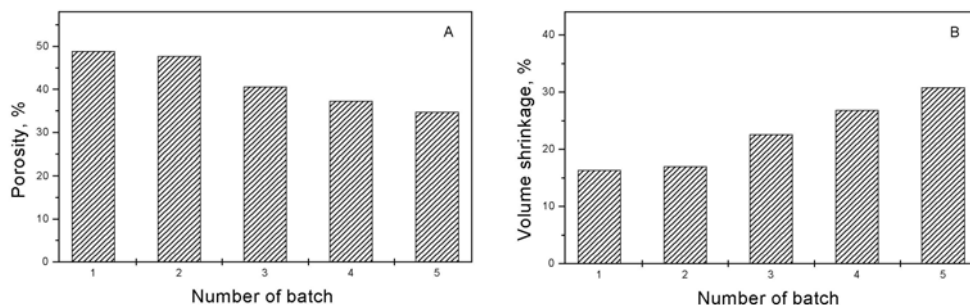


Fig.5. Porosity (A) and volume shrinkage (B) of sintered at 1000°C batches.

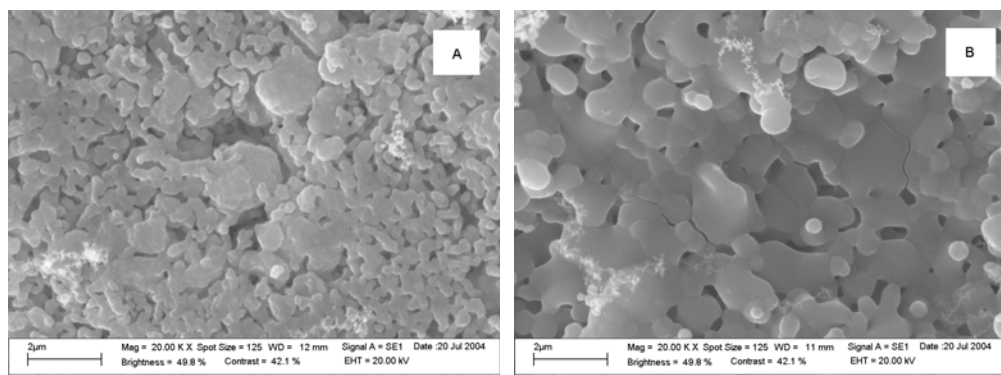


Fig.6. SEM micrograph of ceramics: A – batch 1, B – batch 5.

CONCLUSIONS

The thermal decomposition and the sintering of CA ceramics were studied and the following conclusions can be drawn from the results obtained:

1. The AB-type carbonated apatite starts to decompose at a temperature as low as 500°C, releasing both CO and CO₂ into the gas phase, but remaining is an apatite structure and some amount of carbonate substitution, at least up to 1100°C.
2. The densification of the CA ceramics at sintering in an air atmosphere furnace can be enhanced by a sodium orthophosphate additive which, however, significantly induces grain growth. Porous ceramics with submicrometer size pores favorable for a bone tissue replacement application can be fabricated by sintering CA powders at 1000°C, avoiding considerable decomposition of CA.

Acknowledgement

The work was supported by RAS-SAS agreement, bilateral project NT-14, and the Moscow Committee for Science and Technologies grant n 1.1.58.

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