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Carbonate release from carbonated hydroxyapatite in the wide temperature rage

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Abstract Synthetic carbonated apatite ceramics are considered as promising alternative to auto- and allograft materials for bone substitute. The aim of this study was to investigate the thermal stability of an AB-type carbonated apatite in the wide temperature range. The data on the thermal stability have to allow the conditions of the sintering of the ceramics to be controlled. Initial carbonated apatite powders were prepared by interaction between calcium oxide and ammonium hydrogen phosphate with addition of ammonium carbonate. Decomposition process was monitored by infra red spectroscopy, weight loss and X-ray diffraction of solid, and by infra red analysis of condensed gas phase resulted from the thermal decomposition of the sample in equilibrium conditions. Features of carbon monoxide and carbon dioxide release were revealed. The synthesized AB-type carbonated apatite is started to decompose at about 400°C releasing mainly carbon dioxide, but retained some carbonate groups and apatite structure at the temperature 1100°C useful to prepare porous carbonate-apatite ceramics intended for bone tissue engineering scaffolds.

1. Introduction

The development of bioactive ceramics as alternative to allograft or autograft would be a major advance in biomedical materials science and technology [1, 2]. Human bone mineral differs in composition from stoichiometric hydroxyapatite (HA), being always carbonate-substituted apatite. Content of carbonate in the bone varies from about 2 to 8 wt. % depending on the individual's age [3, 4], The carbonate ion can competitively substitute at two sites in the apatite structure, namely the hydroxyl and the phosphate ion positions, giving A- and B-type carbonated apatite (CA), respectively [5]. These two types of substitution can occur simultaneously, resulting in a mixed AB-type substitution [6, 7]. The apatite that constitutes bone mineral is considered to be always of AB-type, the share from the B-type substitution being predominant over A-type [1, 8, 9].

The carbonate loss at the sintering of CA-ceramics must be controlled in order to assure the carbonate amount necessary for adequate biological behavior of graft. Therefore, the thermal stability of CA powder seems to be a key problem. Relatively little is known about the thermal stability of CA [1, 9–12]. The heat-treatment experiments were performed in various gas atmospheres, including nitrogen, carbon dioxide, air, water vapor and wet oxygen. The gas atmosphere was revealed to affect the decomposition significantly. When AB-type CA was heat-treated in an air atmosphere, phase decomposition occurred at temperature as low as 750°C [1]. B-type CA was revealed to decompose into apatite and calcium oxide in air at temperatures above 1000°C [10]. A mechanism was

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proposed showing the way in which CA can lose some CO_2 without phase decomposition occurring until a critical point is reached where sufficient CO_2 is lost [1]. Sintered in wet carbon dioxide atmosphere, the B-type CA did not show any evidence of decomposition at temperatures up to 1300°C [10, 12]. Besides the heat-treatment atmosphere composition, the thermal behavior of CA can be supposed to depend on the synthesis technique and route [1]. The data reported were obtained mostly on the samples which have been synthesized by wet techniques of precipitation from solution [9, 10, 12].

The study of the thermal stability in an equilibrium condition is needed as a starting point. With this respect, the present work was aimed at the investigation of thermal decomposition of the AB-type CA by Fourier transformed infra red (FTIR) spectroscopy analysis of the carbon oxides in the gas phase in the wide temperature range, by thermal analysis of weight loss (TG), and by monitoring of residue by FTIR and X-ray diffraction (XRD) of solid. The CA was prepared using a technique which differs from common ones.

2. Materials and methods

2.1. Materials

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

$$10CaO + 6(NH_4)_2HPO_4 + (NH_4)_2CO_3 + 4H_2O$$
$$\Rightarrow Ca_{10}(PO_4)_{6-y}CO_3(OH)_{2-z} + 14NH_4OH; 3y + z = 2$$

Initial reagents (analytical grade) were mixed at equimolar ratio (28 g CaO, 39.6 g $(NH_4)_2HPO_4$ and 4.8 g $(NH_4)_2CO_3$), according to the reaction above, in a planetary ball mill for 30 min. After that, 300 ml H_2O 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 [13]. The reaction product, white powder, was then subjected to the heat treatment at 300°C in an air atmosphere furnace.

2.2. 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 reaction between sample and hydrochloric acid [14].

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 decomposing sample consists of a cooling system-cryotype (Displex, Air Products and Chemicals 202 CSA) located in a home made high vacuum stainless steel shroud-connected under rotary vacuum to a Bruker IFS 113 v Interferometer through a suitable IR-transparent CsI window.

The CA samples have been vaporized in equilibrium conditions from tantalum Knudsen cells having orifices of 1 mm in diameter. In order to heat the cell, a tantalum liner was used. It was resistively heated by two water cooled copper electrodes connected to a power supply. A gold-plated cold finger is located in a vacuum chamber connected under high vacuum to the high temperature furnace. The cold finger was allowed to rotate providing two reflecting surfaces, so one can carry out 2 series of measurements during the same experiment. Matrix gas and evaporating species were condensed at $T \approx 12$ K on the gold-plated cold finger. Details of the apparatus are described elsewhere [15].

High-purity argon was used as isolating matrix gas with the flow rate of 1–1.5 mmol/h through a standardised needle valve. Each sample (about 100 mg) in the form of powder was loaded into the cell of 1 cm^3 volume and vaporized. The system was kept under vacuum for several hours before the measurements are started. The vaporization temperature was increased by steps of 150°C in the range of 180–1600°C. For sake of comparison, the same period of time was adopted for all depositions. Depositions lasting 15 min were performed after temperature reached a gives value (the temperature increase lasted about 5–10 min). After the deposition, the temperature was decreased to room tempearture and the spectrum was recorded in reflection mode. About 200 scans were accumulated with a resolution of 1 cm^{-1}. Blank spectra have been recorded with 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 $\lambda = 1.54056$ Å, scan type: continuous; scan step size 0.01671 deg; time per step: 2 s; number of points: 5386). Lattice constants, a and c, were calculated by least squares refinements, using equations for hexagonal cell (space group $P6_3/m$) given in [16]. A homemade PC program, which is somewhat similar to the RLC-3 program, was employed in calculations. High-purity silica was used as an internal standard.

TG measurements were performed using a Thermobalance Ugine Eyraud Setaram B 60 apparatus, consisting of a vertical furnace (25 mm in diameter and 600 mm long) in a graphite heater, under vacuum of 10^{-5} Pa provided by a diffusion pump. A quartz furnace was used in the 20–1100°C temperature range, whereas the heating to 1500°C was performed in an alumina furnace. The cell with sample was suspended in the isothermal zone of the furnace with a tungsten wire. The temperature was measured by a Pt-Pt/Rh thermocouple situated below the cell within the 1.5 mm of distance from the bottom of the cell in the isothermal zone. Temperature was increased gradually with the rate of 300°C per hour. The samples were evaporated from the tantalum Knudsen cell having an orifice of 1 mm diameter in the experiments with the heating up to 1100°C. The cells without covers, i.e. cells of free evaporation, were used for the measurements up to 1500°C. The weight of loaded sample was 100–200 mg.

Particle size was evaluated by scanning electron microscopy (SEM) observations using a LEO 1450 microscope.

3. Results and discussion

Initial powder was of white color and mean particle size of about 0.5 μm. The particles were agglomerated into soft granules of about 50 μm mean size. According to chemical analysis, the carbon content in the samples was 1.56 ± 0.2 wt.%, being more than predicted 1.17 wt.%. XRD patterns of the 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. 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]. Besides of CA peaks, the calcium carbonate peaks can clearly be observed at 2 Theta 29.4° and 39.4° for initial powder and after its exposure 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). Therefore, the contribution from $CaCO_3$ to the total carbon content. 1.56 wt.%, in the sample does not exceed 0.04 wt.%.

After exposure to 950°C and above, a diffraction peak at 2 Theta 37.5° was appeared resulting from CaO due to the partial phase decomposition of calcium carbonate and CA structure [1, 10]. Indirectly, the formation of CaO as the decomposition product indicates that the CA was of AB-type having the Ca/P ratio greater than 1.67 [10]. In opposite case of A-type CA, the decomposition products might be tricalcium phosphate and tetracalcium phosphate [17]. 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 its decomposition occurring at this temperature [18]. According to chemical analysis, the carbon content in the sample after exposure to 1000°C equals to 0.42 ± 0.03 wt.%, the carbon loss being of 1.11 wt.%. This carbon content reduction is mainly due to the CA decomposition, because the decomposition of calcium carbonate (3 wt.%) can result in carbon decrease by 0.04 wt.% only.

Fig. 2 shows FTIR spectra of the initial powder (sample 1) and the residues after the heattreatment at 1100°C (sample 2) and 1500°C (sample 3). The spectra provide a number off spectral details indicating some transformations occurred. Hydroxyl groups stretch mode band was observed near 3570 cm^{-1} in the spectrum of sample 1, being disappeared in the spectra of samples 2 and 3. There were v_1 phosphate bands located at 960-962 cm^{-1} in all the spectra. Phosphate v_4 band is present in the 660–520 cm^{-1} region. It has two sites centered at about 600-602 cm^{-1} and 553-563 cm^{-1}, both are characteristics of carbonated HA [19]. Peak at 633 cm^{-1} seems to be very weak, if exists. An intense v_3 band is present near 1030-1080 cm^{-1} being splitted into two peaks for sample 1. This band was transformed significantly after the thermal exposure, especially at 1500°C.

Peaks in the region of 1650 to 1300 cm^{-1} are due to v_3 vibrational mode carbonate ion, and the peak at 873 cm^{-1} is due to the carbonate v_2 vibrational mode [19]. The ratio of v_3 carbonate band area to v_3 phosphate band area is known can be used as a measure of carbonate/phosphate ions ratio [19]. It can be concluded from the spectra given in Fig. 2 that the CA samples retain the carbonate groups after being exposed to 1100°C, but carbonate was mostly lost at 1500°C. Only low intensity band at about 870 cm^{-1} indicates that some amount of carbonate is still retained.

According to [9], strong peaks at 870, 1430 and 1450 cm^{-1} correspond to the B-type CHA, whereas the typical peaks of the A-type CHA are centered at 880, 1450 and 1540 cm^{-1}. The existence of peaks at 870-880 cm^{-1}, 1450 and 1540 cm^{-1} is evident for the sample 1. Keeping in mind the presence of weak hydroxyl band at 3570 cm^{-1}, one can conclude that the intial sample consists of the CA of AB-type. After exposure to 1100°C three peaks at 1405 to 1544 cm^{-1} were transformed into a wide band centered at 1440 cm^{-1}, and no splitting of the peak at 876 cm^{-1} was observed. It is known that the occupancy of the v_2 sites occurs competitively between the OH^- and carbonate groups, whereas occupancy of the v_3 sites depends on competition between the phosphate and carbonate ions [19]. Thus, the presence of intense v_3 carbonate bands in the region of 1400-1460 cm^{-1} and v_2 band at about 870 cm^{-1}, and the absence of hydroxyl stretch band lead to opinion that the exposure at 1100°C resulted in the formation of AB-type CA.

Figure 3 shows CO and CO_2 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 (which is not always presented) at 2142.5 cm^{-1}. The highest frequency fundamental is attributed to the isolated molecule [20–24], while the interpretation of remaining bands is at present not univocal.

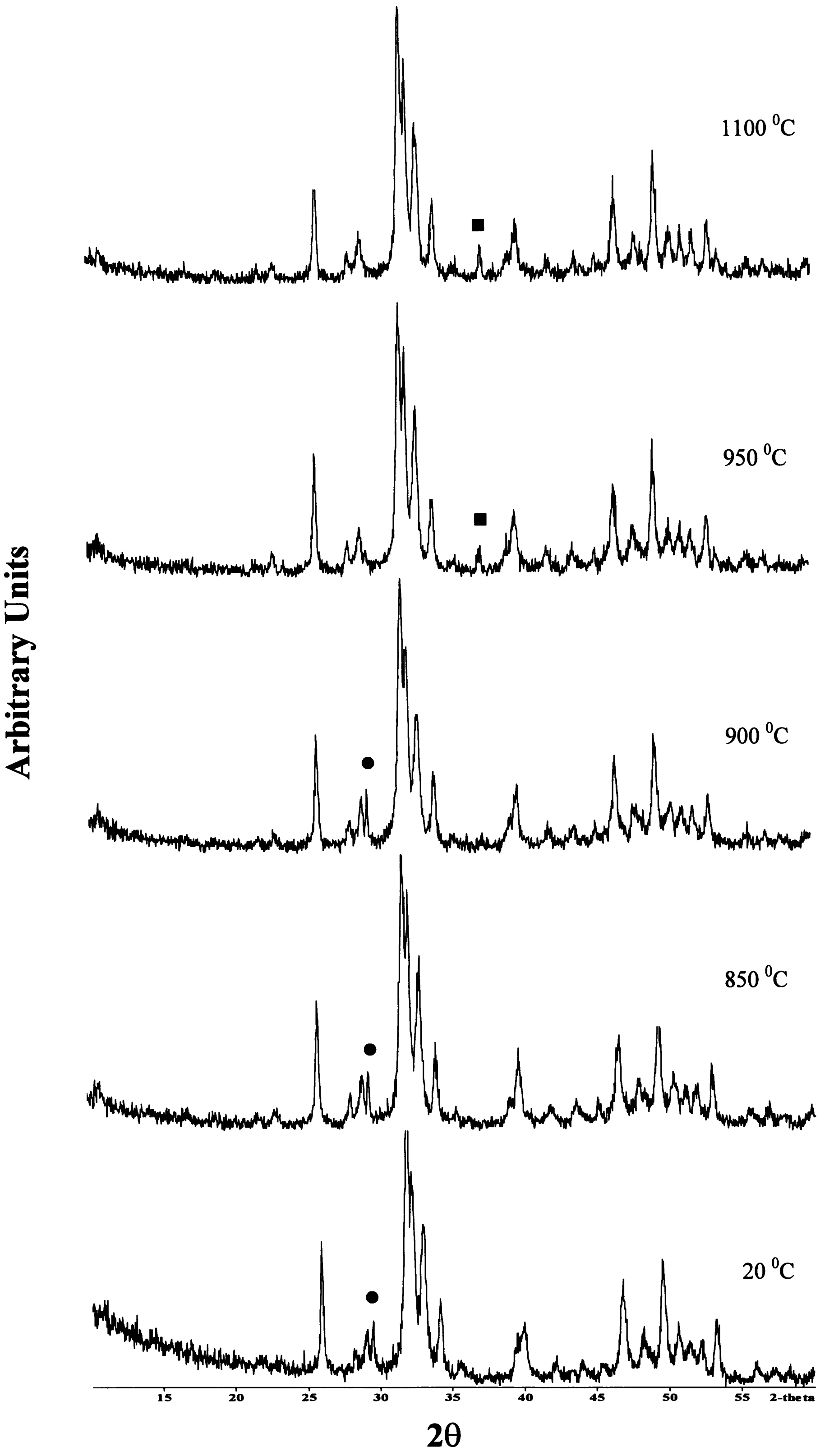


Fig. 1 XRD patterns of CA powder at 20°C, 850°C, 900°C, 950°C and 1100°C. ●- calcium carbonate; ■ - calcium oxide.

Fig. 2 FTIR spectra of initial CA powder (a), residues after exposure to 1100°C (b) and to 1500°C (c).

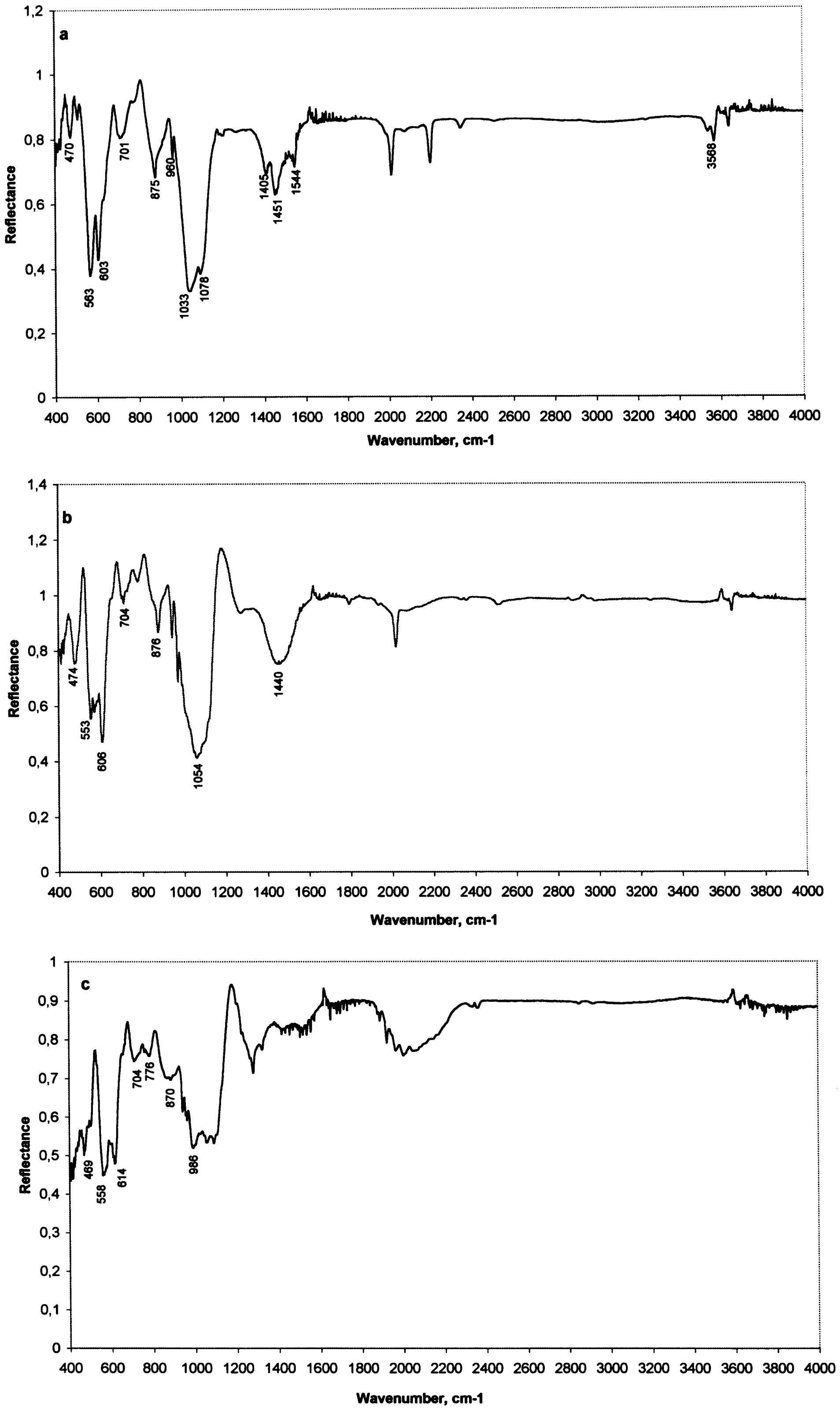
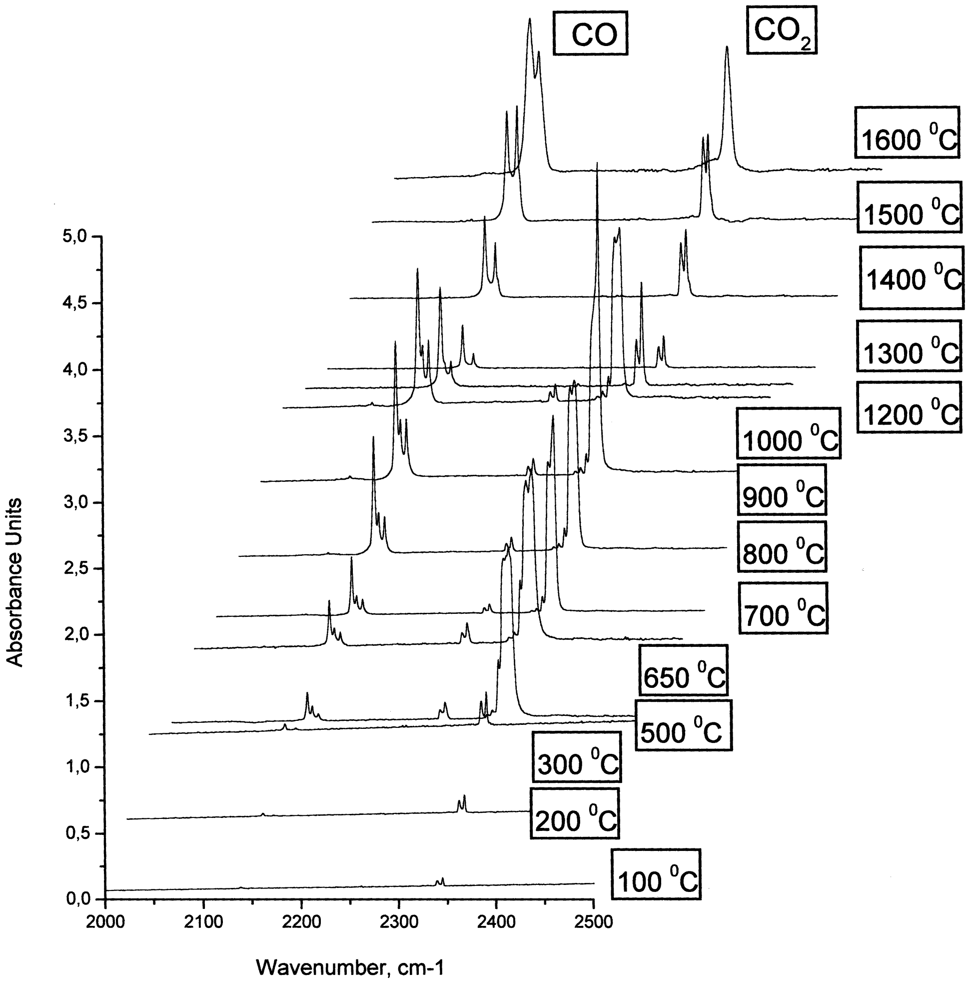


Fig. 3 CO and CO_2 bands in FTIR spectra of gaseous phase released from CA in the wide temperature range.



In fact, different assignments have been proposed including association, libration or interaction with molecules polluting the matrix [21–24]. In particular, the assignment of the band at 2142.5 cm^{-1} is uncertain considering that its random appearance cannot be connected to a given experimental parameter. In our spectra the bands at 2148.9 and 2138.2 cm^{-1} gain intensity with the vaporization temperature at different rates. The latter, in fact, grows much faster and predominates at high vaporization temperature which produces less isolating conditions. This behaviour suggests the attribution of the band at 2138.2 cm^{-1} to an aggregate of CO molecules. The calculated area, which could be considered as a measure of content, of the CO band *versus* vaporization temperature is shown in Fig. 4a. It becomes clear that CO evolution starts at about 500°C, goes through a maximum at about 1000°C, and increases rapidly above 1300°C.

The bands at 2344.8 and 2339.4 cm^{-1} are assigned to the asymmetric stretching mode of CO_2. The doubling has been attributed to the existence in argon of two acceptable sites for the carbon dioxide molecules [24]. Trend in the CO_2 peak area *versus* vaporization temperature differs from that revealed for the CO band (Fig. 4b). Plots evidence that two maximums are reached in the temperature range from 500 to 800°C followed by rapid decrease in CO_2 evolution with a minimum at about 1300°C. Therefore, it can be concluded that the primary product of the CA decomposition is carbon dioxide. The released CO_2 decomposes into CO and oxygen with a rise of temperature due to the decomposition reaction rate constant increases with temperature [25]. The presence of wide ν_3 carbonate band in residue at 1440 cm^{-1}, as well as the XRD data, indicate that some carbonate groups are still retained their position as phosphate substitute, at least up to 1100°C. No calcium carbonate which could cause the CO_3 absorption peaks in IR spectrum of residue was revealed by XRD at this temperature. Over 1300°C the CA decomposes rapidly, the process being accompanied by a sharp growth in both the CO and the CO_2 peaks area, and only low intensity carbonate band at 870 cm^{-1} was revealed by FTIR of solid residue heated at 1500°C.

Shown in Fig. 5 are TG curves of initial powder (Fig. 5a) and that recorded at re-heating of the sample which has been initially tested in the temperature range from a room temperature to 1100°C (Fig. 5b). A decrease of weight on the heating up to about 500°C can be attributed mainly to the

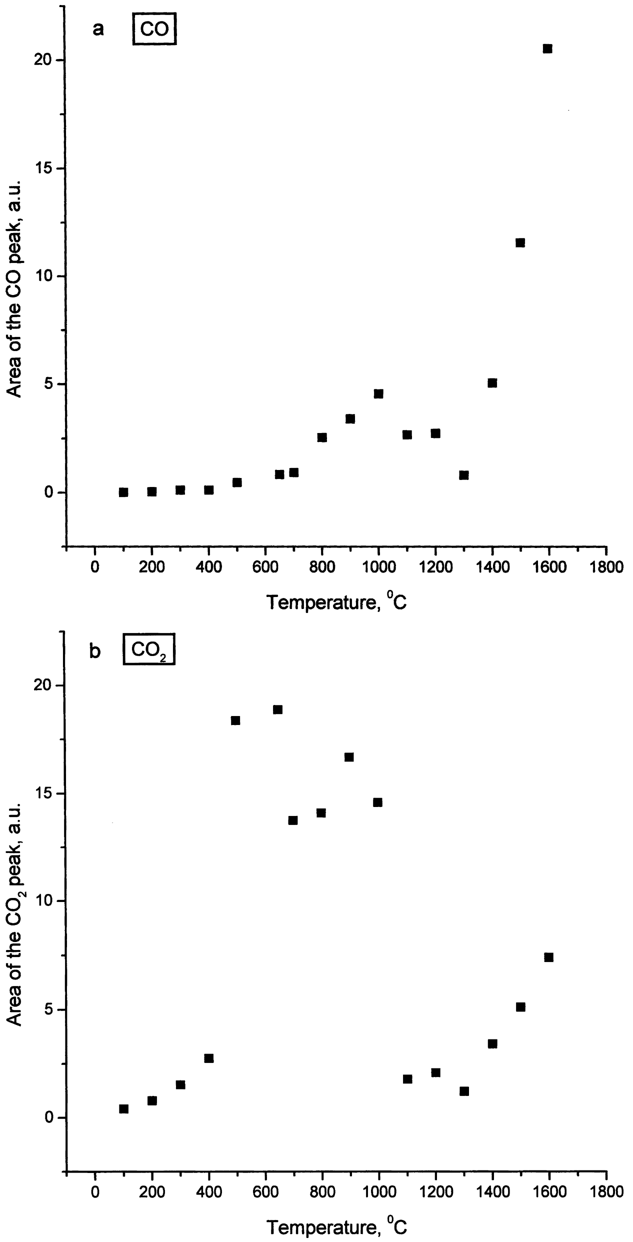


Fig. 4 Area of CO (a) and CO_2 peaks *versus* vaporization temperature.

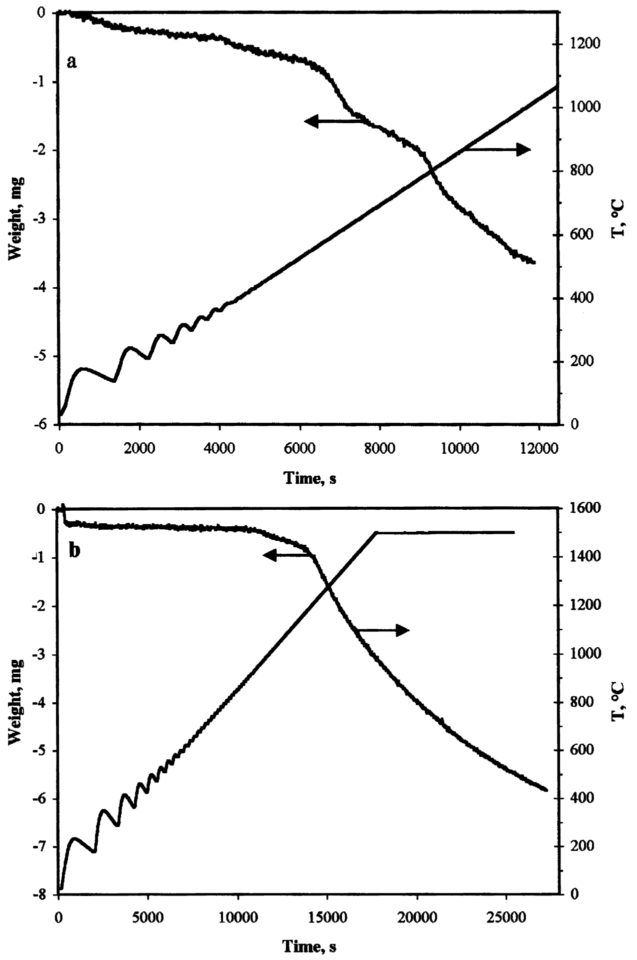


Fig. 5 TG plots for heating of initial powder (a) and for re-heating of residue exposed to 1200°C.

loss of adsorbed and lattice H_2O. Further increase in slope corresponds to the FTIR data on carbon dioxide release. In the range from about 660°C to 800°C the rate of the weight loss decreases, in accordance to the trend in the CO_2 FTIR peak area. The second increase in the slop occurred at about 800°C, accompanying by the rise in CO evolution (Fig. 4a). At last, the third crucial temperature in the CA decomposition is about 1250°C when the CA begins to decompose rapidly. Thus, the thermal decomposition of the CA includes at least three stages starting from water release followed probably by the loss of carbonate substituted for OH and, further, by the release of carbonate substituted for phosphate groups. It should be noted that the CA prepared in accordance to our semi-dry synthesis method seems to be more stable compared to that prepared by a common wet synthesis using calcium nitrate and solutions of hydrogen phosphate and carbonate salts as the starting reagents. This allows to increase the sintering temperature of CA up to about 1100°C compared to that of about 750°C [26], remaining carbonated apatite phase which is favourable for the biological response of the bone substitute material. Even if the sintered ceramic body becomes porous, so it could be used as scaffold for stem cells or bone morphogenetic proteins in tissue engineering technologies. The results of this study could also be employed in development of the sintering route for CA-ceramics, in particular to control properly the gas atmosphere (controlled CO_2/CO ratio) to suppress the evolution of certain carbon oxide during the sintering.

4. Conclusions

Carbonated apatite of AB-type has been synthesized using calcium oxide, ammonium hydrogen phosphate and ammonium carbonate as starting reagents. The thermal stability of the product was studied in the wide temperature range. The following conclusions can be drawn from the results.

1. The CA is started to decompose at about 400°C releasing mainly carbon dioxide. Carbon monoxide content in the vaporization atmosphere begins to rise at about 800°C. Changes in the CO_2/CO ratio in the vaporization atmosphere occur non-monotonously with an increase in the thermal decomposition temperature. It should be accounted for the development of the sintering route in a protective carbon oxides gas atmosphere.
2. At least three stages of the decomposition process were revealed, probably due to the water loss, A- and B-type substituted carbonate groups loss, consecutively.
3. The AB-type CA retains its apatite-type structure and partly the carbonate groups at 1100°C, the temperature being useful to fabricate porous CA-ceramics.

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