Solid solution formation at the sintering of hydroxyapatite–fluorapatite ceramics

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Received 9 February 2004; revised 25 February 2004; accepted 26 February 2004
Available online 17 April 2004

Abstract

Fluorohydroxyapatite ceramics are increasingly studied for the use as biomaterials due to their good integration ability in the bone tissue and higher resorption resistance compared to the common hydroxyapatite (HA) ceramics. This study is aimed at the X-ray diffraction investigation of the interaction between HA and fluorapatite (FA) particulates in the sintering temperature range up to 1300 °C. The lattice parameters were calculated in dependence of both the FA content in the powder mixtures and the sintering temperature. From those data, the solid solution formation is concluded, at least in the temperature range from 1200 to 1300 °C. Energy-dispersive X-ray microanalysis confirmed the fluorine distribution to be almost uniform in the sintered at 1300 °C ceramics.

Keywords: Biomaterials; Hydroxyapatite; Fluorapatite; Solid solutions; Ceramics

1. Introduction

The mineral phase of hard tissues contains significant amount of fluorine ions, being partially substituted for OH− groups in the apatite structure of this phase [1,2]. Fluorine ions are believed to improve stability of hydroxyapatite (HA) in the biological environments [3,4], positively affecting bone cell proliferation [5]. Partially fluorided hydroxyapatite (FHA) and fluorapatite (FA) crystals have been found in bone tissue and dental enamel, respectively [6]. The physiological significance of fluorine ions is the reasons why synthesis and detailed investigation of fluorine-containing apatite attracted substantial attention during the last decade [6–12]. Introduction of fluorine into the HA can be achieved using various approaches. FHA can be fabricated by the reaction between solid HA and NaF solution [4]. Alternatively, solid-state interaction between HA and ammonium fluoride at a high temperature can provide an FHA [13]. Another route is the solid state reaction of HA with calcium fluoride [7]. FHA can be obtained by the hydrolysis of tetracalcium phosphate in potassium hydrogen phosphate solution in the presence of potassium fluoride [14]. All these methods possess some advantages and shortcomings. Recently, a simple route to prepare HA–FA granules has been described, the method being based on the mixing of HA and FA fine powders, the dispersion of well-mixed powder/gelatin mixture in a dispersion medium to prepare the rounded raw granules, followed by the heat treatment to harden the granules and to burn-off the gelatin [15]. These porous ceramic granules can find wide application as scaffolds for bone tissue engineering or matrices in drug delivery systems. The uniformity of fluorine distribution in these ceramic bodies is in question. Preliminary IR spectroscopy study demonstrated the possibility of solid solution formation between HA and FA at the sintering temperature of 1200 °C: the C3v–OH vibrational mode band shifts to 637 cm−1 indicating the partial fluorine substitution for OH− groups. From the other hand, the FA can be transformed into fluoroxyapatite at a high temperature [16]. Therefore, further study is needed to ascertain the features of the interaction between HA and FA at high temperatures, which are usually employed to prepare the HA-base ceramics. In this context, the present work was aimed at the X-ray diffraction study of solid solution...
formation in the HA–FA particulate systems during the sintering in the temperature range up to 1300 °C.

2. Materials and methods

The HA material was prepared by precipitation from aqueous solution technique. The analytical grade Ca(NO₃)₂, (NH₄)₂HPO₄ and NH₄OH were used as the starting reagents. The synthesis reaction is as follows:

\[ 10\text{Ca(NO}_3\text{)}_2 + 6(\text{NH}_4\text{)}_2\text{HPO}_4 + 8\text{NH}_4\text{OH} \]
\[ \Rightarrow \text{Ca}_{10}\text{(PO}_4\text{)}_6(\text{OH})_2 + 20\text{NH}_4\text{NO}_3 + 6\text{H}_2\text{O} \]

Raw product of the reaction, white powder, was calcined at 900 °C for 6 h in an air furnace. The characteristics of the calcined product were as follows: Ca/P = 1.67 (wet chemical analysis); BET specific area as determined by nitrogen gas adsorption (a Quantachrome Autosorb) is about 5.2 m²/g; median powder agglomerate size is about 2.2 μm (a Coulter Counter); density is 2.16 g/cm³.

The FA powder was obtained by solid state interaction as follows:

\[ 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaF}_2 \Rightarrow \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \]

The reaction has previously been studied in Ref. [7]. Analytical grade reagents were used. The mixture of Ca₃(PO₄)₂ with CaF₂ in equimolar ratio (Ca/P = 1.67) was subjected to the milling in a ball mill at the ratio of 1:3 (powder:balls) with ethanol addition for 6 h. After that the mixture was calcined at 600 °C for 3 h in a furnace with air atmosphere, followed by milling and heat treatment at 1100 °C for 2 h in a dry nitrogen atmosphere. The particle size of the powder was estimated from scanning electron microscopy (SEM) measurements (a JEOL JSM-35-CF microscope). The submicron dimension individual particles were agglomerated into the large particles of 2–10 μm size. Ca/P ratio is equal to about 1.67 (wet chemical analysis data). The product contains 3.8 wt% F⁻, which is close to the predicted value of 3.96 wt%. BET specific area of the powder was about 13 m²/g. The phase composition was identified by comparing the diffraction patterns (a DRON 3 diffractometer) with peaks given in database ICDD PDF (cards #09-0432 for HA and #15-0876 for FA). The products are proved to correspond to the HA and the FA, respectively.

The mixtures of HA with 2, 10 or 50 wt% FA were prepared in a planetary ball mill using an ethanol media and corundum balls at the batch-to-balls ratio of 1:4. The mixing time was 2 h. After drying at 90 °C and granulation using a standard sieve of 400 μm cell, the batches were uniaxially pressed in a hardened steel mold under the pressure of 150 MPa, followed by heat treatment in an air furnace at 800 (HA and FA only), 1150, 1200, 1250 and 1300 °C for 2 h. The samples were discs of about 14 mm diameter.

Microstructure of the samples was observed by SEM using a LEO 1450 VP microscope coupled with an EDX microanalysis system INCA 300 to determine the fluorine distribution. X-ray diffraction (XRD) experiments were performed by powder method using a DRON 3 diffractometer (Cu Kα radiation, scanning speed 0.5 deg/min). To minimize an error related to sample preparation, the diffraction patterns were registered for three samples of the same mixture, each sample was prepared by independently filling the sample holder. Lattice constants, a and c, and volume of cell, V, were calculated by least squares refinements from the well-determined positions of ‘mass centre’ of the reflections, using equations for hexagonal cell (space group P6₃/m) given in Ref. [17]. A home-made PC program, which is somewhat similar to the RLC-3 program, was employed in calculations. High-purity silica was used as an internal standard. Three-to-five measurements were made for each sample. The averaged chemical analysis was performed by a laser mass-spectrometry method (a EMAL-2 analyser). The samples were also characterized for open pores content by Archimedes method of hydrostatic weighing in distilled water.

3. Results and discussion

XRD on the heat-treated powders indicated that a single-phase apatite was formed for all fluoride concentration powders, excepting those containing up to 50 wt% FA and subjected to heat-treatment at a temperature under 1300 °C. The samples heat-treated at 1300 °C contain traces of beta-tricalcium phosphate (TCP) in amount up to about 2 wt% estimated by comparing the ratio of the areas of the most intense diffraction maxima 211 HA and 0210 β-TCP with those in standard HA/β-TCP plot. The change in peak position accompanied by FA addition to the HA was detected, which is characteristic of FHA formation. The peaks 300 and 410 were shifted to higher diffraction angle, whereas position of the peaks 002 and 004 was changed towards lower angle with an increase in FA content at a certain heat-treatment temperature.

Given in Table 1 are the results of calculation of the lattice parameters and cell volume for all the samples. The lattice constants of pure HA generally correspond to the data reported in Ref. [18]: \( a = b = 9.432 \text{ Å} \) and \( c = 6.881 \text{ Å} \), both values being just a little bit smaller. The value of \( a \) is in good agreement with that of \( a = 9.4155 \text{ Å} \), reported in Ref. [7]. The measured lattice constant values of FA are very close to those reported in Ref. [7]: \( a = 9.3716 \text{ Å} \) and \( c = 6.884 \text{ Å} \).

Fig. 1 shows the lattice constants and the cell volume dependence on the FA content in the samples sintered at different temperatures. A change in the \( a \) lattice parameter can obviously be noted, whereas the \( c \) lattice parameter does not show any discernable difference. The \( a \) parameter decreases markedly with increasing fluorine content.
This result is in agreement with the data on dependence of $a$ on degree of fluoridation in both the precipitated and the sintered FHAs [6,19]. Therefore, the solid solution HA–FA formation can probably be concluded from these data, also keeping in mind that the IR spectroscopy study results have been reported in Ref. [15]. The slope of the $a$ and $V$ versus FA content plots depends on the heat-treatment temperature. Given in Fig. 2 is the dependence of the lattice parameters on the heat-treatment temperature for the samples of different FA content. The lattice parameters of FA are practically independent of the heat-treatment temperature, due to this FA is the most stable compound among the apatites [20]. Contrary to the FA, the dependence of $a$ on the heat-treatment temperature for both the pure HA and the HA–FA mixtures goes through a minimum, which is located at about 1200 °C. Non-linear dependence of $a$ on sintering temperature could also be noted from the results reported by Ref. [6]. Generally, the decrease in the lattice parameter is indicative of a denser structure produced by the higher sintering temperature, in our case up to 1200 °C [6]. The lattice shrinkage can be supposed to result from (i) the ordering and the increase of the crystallinity index of the structure, (ii) the effect of dehydroxylation [21], and (iii) a trend towards the formation of oxyapatite of smaller lattice parameters after heating than those of HA [22]. Further increase of the lattice parameter $a$ and the unit cell volume with temperature above 1200 °C can probably be attributed to the rising instability of the HA lattice before its transformation to the beta-TCP lattice accompanied by the reduction in symmetry from hexagonal to monoclinic of larger lattice constants ($a = 12.887$ Å, $b = 27.280$ Å, $c = 15.219$ Å) compared to those in pure stoichiometric HA, which can also be described as monoclinic [20]. This phase transformation related to the hydroxyl group loss.

| Sample | Lattice constants | ICDD data* | Heat-treatment temperature (°C) |
|--------|------------------|------------|---------------------------------|
|        | $a$, Å            | $c$, Å     | $V$, Å³                         | 800 | 1150 | 1200 | 1250 | 1300 |
| HA     | 9.4180            | 6.8840     | 528.41                          |     |      |      |      |      |
|        | 9.417(2)          | 6.879(2)   | 527.20                          |     |      |      |      |      |
|        | 9.405(1)          | 6.881(1)   | 527.87                          |     |      |      |      |      |
|        | 9.396(1)          | 6.877(2)   | 526.15                          |     |      |      |      |      |
|        | 9.399(1)          | 6.878(1)   | 526.69                          |     |      |      |      |      |
| HA-2FA | 9.404(2)          | 6.881(1)   | 527.00                          |     |      |      |      |      |
|        | 9.396(1)          | 6.878(2)   | 525.83                          |     |      |      |      |      |
|        | 9.398(3)          | 6.878(1)   | 526.10                          |     |      |      |      |      |
|        | 9.402(2)          | 6.878(1)   | 526.54                          |     |      |      |      |      |
| HA-10FA| 9.401(1)          | 6.880(1)   | 526.58                          |     |      |      |      |      |
|        | 9.394(1)          | 6.878(1)   | 525.63                          |     |      |      |      |      |
|        | 9.3968            | 6.8785     | 525.98                          |     |      |      |      |      |
|        | 9.400(1)          | 6.879(1)   | 526.39                          |     |      |      |      |      |
| HA-50FA| 9.3684            | 6.8841     | 523.98                          |     |      |      |      |      |
|        | 9.372(1)          | 6.885(1)   | 523.80                          |     |      |      |      |      |
|        | 9.373(2)          | 6.884(5)   | 523.65                          |     |      |      |      |      |
|        | 9.372(1)          | 6.884(2)   |                                 |     |      |      |      |      |

Standard deviations in units of the last significative figure are given in parentheses. *ICDD PDF No. 09-0432 and No. 15-0876 for synthetic HA and FA, respectively.
Fluoride substitution for OH$^-$ group may stabilize the HA structure making the rise of the lattice constant $a$ with temperature above 1200 °C not so intensive, as it can be seen for the HA–50 wt% FA sample.

Scanning electron micrographs of HA-10 wt% FA ceramics sintered at 1200 and 1300 °C are shown in Fig. 3a and b, respectively. Even at high magnification, no significant difference of atomic contrast is observable in the samples’ image obtained through backscattered electrons detection, as a proof of the high homogeneity of the samples. Open pore content in ceramics decreases from 25.2% down to 1.4% with an increase in the sintering temperature in this range. Averaged fluorine content in ceramics equals 0.65 wt%, according to laser mass spectrometry data. The results of the local EDX analysis performed at many points (about 20) on the surface of the sample sintered at 1300 °C were in the range from 1.08 to 0.41 wt%, the mean being 0.74 wt%, i.e. close to that determined by laser mass spectrometry. No fluorine-free points were detected by EDX punctual analysis, even at high magnification and by using a small divergence of the electron beam. These data confirm the solid solution formation at a temperature, at least, as high as 1300 °C. It was impossible to perform EDX analysis at lower temperatures of the heat treatment due to the roughness of the surface of samples.

Thus, the XRD and EDX studies confirm the possibility of solid solution formation in the HA–FA particulate systems in the temperature range useful for sintering of FHA ceramics.

**4. Conclusion**

The XRD experiments were performed with the HA-base ceramics sintered at 1150–1300 °C containing up to 50 wt% FA. The following conclusions can be drawn from the results.

1. The lattice constant $a$ and the unit cell volume decrease with an increase in FA content at a certain heat treatment temperature in the range from 1150 to 1300 °C indicating possible solid solutions formation between HA and FA. This possibility is confirmed by the local EDX analysis performed at many different points on the surface of
the sample sintered at 1300 °C. Effect of the heat treatment temperature on the change of the lattice constant $a$ decreases with an increase of FA content.

2. In the heat treatment temperature range above 1200 °C the lattice constant $a$ and the unit cell volume have a trend to be increased, probably due to destabilization of the apatite lattice near the phase transformation of HA to TCP temperature.

Acknowledgements

Financial support available from The Italian Ministry of Foreign Affairs (project n36 NT14) and from RFBR (grant 03-03-32230) is deeply appreciated.

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