

Structural transformations in the α -tricalcium phosphate powders after mechanical activation and subsequent heat treatment

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Abstract. X-ray diffraction analysis of the structural phase evolution in the α -TCP powder subjected to milling in the planetary mill in butanol, and followed by annealing at 1300 °C was performed. After milling, there was a systematic smoothing of the X-ray diffraction pattern of α -TCP. Significant changes in lattice constants and atomic parameters were not observed. The average particle size was reduced from 10 to 2 micrometers. The decrease of the size of coherently scattering domains CSD (250 to 80 nm) makes the main contribution to the X-ray lines broadening. The value of microstrain changes from $1 \cdot 10^{-6}$ to $2 \cdot 10^{-4}$. After annealing at 1300 °C for 2 hours the phase with apatite structure was found. The content of the apatite phase increases with increasing of time of mechanical activation. Possible mechanisms of deformation of α -TCP particles and structural transformations α -TCP \rightarrow HA are considered.

1. Introduction

Tricalcium phosphate (α -TCP, α -Ca₃(PO₄)₂) represents a large family of phosphate-materials based on bioceramics [1]. On the phase equilibrium diagram CaO-P₂O₅ there are three polymorphs corresponding composition of Ca₃(PO₄)₂: α' -TCP, α -TCP and β -TCP. At room temperature β -TCP is stable; at $t \sim 1125$ °C it turns into α -TCP-phase which is stable in the temperature range 1125-1470 °C. α -TCP is usually prepared by heating β -TCP above $\alpha \leftrightarrow \beta$ transformations. The structure of α -TCP crystallizes in space group P2₁/a with Z=24 (figure 1a). Due to a good solubility α -TCP is applying as a component of the cement used for filling bone defects including metal biomaterials with bone tissue. When interacting with water α -TCP forms a calcium-deficient hydroxyapatite Ca₉(PO₄)₅(HPO₄)(OH) (Figure 1b) that enhances the biocompatibility of cements. It is well known that the dissolution of α -TCP powders in liquids during the manufacturing of cement is controlled primarily by surface reactions, which depend on the rate of dissolution of the powders. There are different ways to increase the dissolution rate, and the most common - increasing the contact surface of the particles with the liquid by milling. The factor stimulating dissolution of particles, is also a grinding of microblocks. In this regard, very relevant to research the changes of dispersion, phase composition, characteristics of the microblock, parameters of the crystal structure in α -TCP powder produced by milling and subsequent annealing typically used to optimize the structure of α -TCP powders. The purpose of this work is the study by X-ray diffraction analysis of structural changes in α -TCP powder, which was



treated in a planetary mill, and subsequently annealed at temperatures corresponding to its stability on the diagram CaO-P₂O₅.

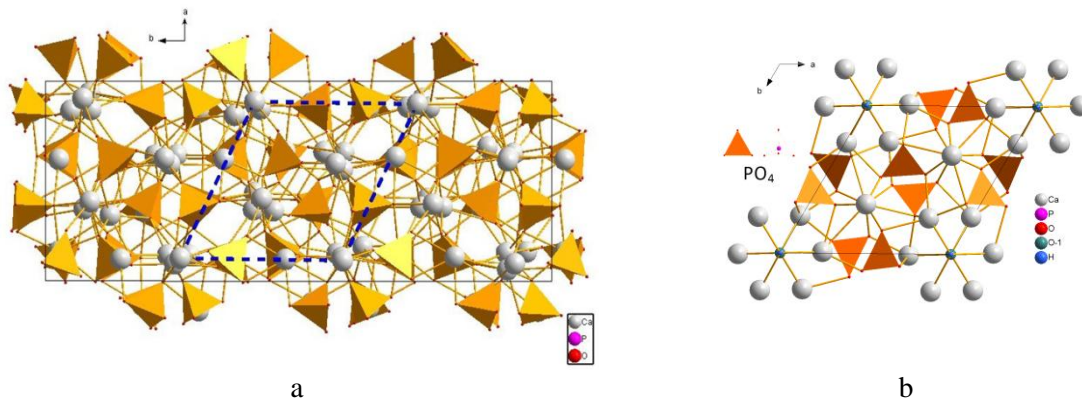


Figure 1. Structure of α -TCP (a) and hydroxyapatite (HA) (b).

2. Experimental

Single-phase α -TCP powder was processed in a planetary mill for 15, 30, 60, 120 and 180 minutes in butanol at 60 °C and subsequent annealing at 1300 °C for 2 hours. Changes in the structure of α -TCP and microblock structure of powders were investigated using the X-ray diffractometer Rigaku Ultima IV in Cu-K α radiation. The phase analysis is performed by means a software package PDXL. Refinement of the crystal structure parameters and microblock structure by the Rietveld method performed using software packages Jana 2006 and MAUD in the two-phase approach. As result, the volume fractions of α -TCP and phases formed during processing in a planetary mill was obtained.

Particle size determination by laser diffraction method was performed. The automatic unit Hydro 2000S and isopropanol alcohol as a dispersant were used.

1. Results and discussion.

In the X-ray pattern of the raw α -TCP powder, there are only reflections corresponding to α -TCP phase with $a=1.2878$, $b=2.7271$, $c=1.5215$ nm, $\beta=126.19^\circ$ (Figure 2).

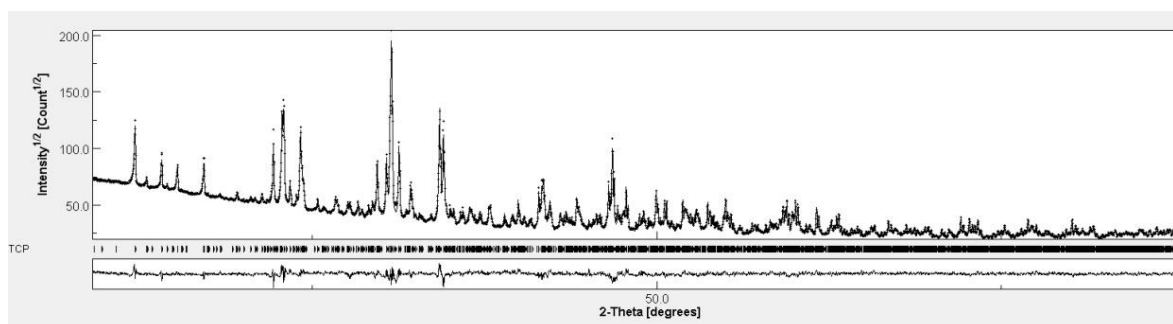


Figure 2. The XRD diffraction pattern of the raw α -TCP powder.

The best correspondence of the diffraction peaks on X-ray diffraction pattern and their intensities and 2θ angles calculated during the refinement of the structure of α -TCP by the Rietveld method was observed with the card ICDD №70-364. Refinement the general parameters (background, shape parameters of lines, their asymmetry, texture March-Dollase parameters) atoms positions and thermal parameters was performed. As an initial atomic coordinates the values given in [2] were used. Refinement of Ca and P coordinates has not resulted in a significant change in their values. Coordinates of oxygen atoms were not refined. In general, the refining structure procedure completed

with $R_{wp} = 6.25$ (Table 1). The broadening of the lines of the XRD pattern is weak, and by hkl essentially does not depend. Subsequently, this sample was used as a standard for estimation of microblock values of powders after mechanical activation.

Table 1. The unit cell parameters α -TCP and the main characteristics of the structure refinement by the Rietveld method.

Parameters specification	Values
a, Å	12,8832
b, Å	27.2837
c, Å	15.2214
β , deg	126.1868
The absolute value of the maximum intensity, imp.	17449
R_{wp} (%)	6.25
R_p (%)	4.62
The number refined the parameters	67
Interval angles 2θ , deg	9-129
Increments for 2θ , deg	0.02
The number of data points	5001
The number of reflections	429

After processing of the powders in the planetary mill a noticeable reduction in grain size was observed (Figure 3). The mean particle diameter, equivalent specific surface area of the grain (D) after treatment for 180 minutes decreased 3.5 times. Such reduction in D and thus increasing their specific surface area leads to an appreciable reduction of solidification time cement [3].

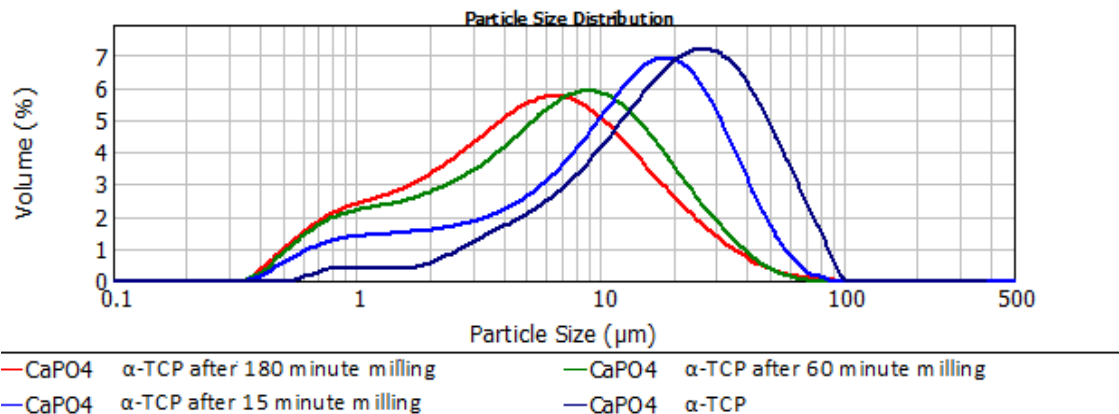


Figure 3. Dimensional distribution of α -TCP particles in size depending on milling time.

In the XRD patterns of powders after milling, the peaks of α -TCP phase are significantly broadened (Figure 4). The relatively weak reflections of $(\text{CF}_2)_n$ phase appear, apparently as a result of interaction powders with the material of the walls of the mill was observed. These results indicate that a significant change of the unit cell values and atomic parameters not happened. Shape anisotropy of microblocks and microstrain were not found. The values of the average size CSD and microstrain (Δ) after the processing of the powder for 60 minutes, where the effect of broadening of X-ray lines was maximal, were respectively: $d \approx 80$ nm; $\Delta \approx 2 \cdot 10^{-4}$ (Table 2). The main contribution to the broadening of the X-ray peaks makes decrease of CSD. Just as in the case of hydroxyapatite, α -TCP plastic deformation perhaps describes as a processes of cluster fragmentation and cluster-boundary “sliding”, the contribution of the plastic deformation by dislocation mechanism is negligible [4].

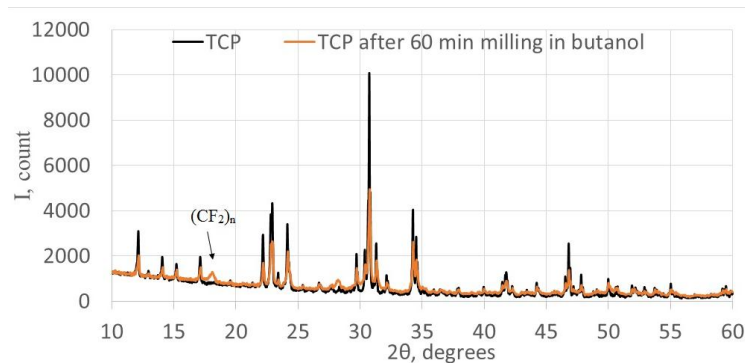


Figure 4. The broadening of the lines α -TCP after 60 min of milling in butanol

The XRD patterns of the samples after treatment in the mill and subsequent annealing at 1300 °C, as it was stated above, contains, as the main phase α -TCP. In addition, the reflexes apatite phase ($a=0.9393$, $c=0.688$ nm) observed. This is most clearly evident in the diffraction XRD pattern of the powder subjected to milling for 180 minutes. From the results of the quantitative phase analysis carried out with the plotting of the calibration curve, it was found that the contents of the apatite phase in powders after mechanical activation and annealing for 60, 120 and 180 min is 47, 58 and 75% respectively. The atomic parameters of apatite phase obtained in refining the structures correspond to the data of [2, 6]. The diffraction spectra of powders were characterized by sharp peaks; microblocks and microstrains contributions in their width is minimized.

Table 2. Content of the phases, the size of CSD of α -TCP, microstrains of α -TCP (Δ) and the refinement factor (R_w) depending on the time of milling of α -TCP (t)

t, min	Content of the phase (%)		CSD (nm)	Δ	R_w (%)
0	α TCP 100		287	2,00E-04	6,25
15	α TCP 98,6	CF ₂ -1,4	172	6,56E-06	6,80
30	α TCP 97,8	CF ₂ -2,2	131	1,89E-05	7,20
60	α TCP 95,8	CF ₂ -4,2	79	2,72E-04	8,92
120	α TCP 95,3	CF ₂ -4,7	127	2,29E-04	6,10
180	α TCP 94,4	CF ₂ -5,6	123	2,19E-04	6,40
After annealing					
60	α TCP 52,6	HA-47,4	222	3,15E-04	9,54
120	α TCP 42,2	HA-57,8	210	2,95E-04	6,54
180	α TCP 24,9	HA-75,1	202	2,34E-04	8,08

The presence in the α -TCP powder apatite phase hydroxyapatite (HA) is usually attributed to the presence of moisture in the air. Therefore, the synthesis under these conditions using phase diagram CaO-P₂O₅-H₂O, which includes phase regions comprising apatite [5]. The transition of α -TCP→HA facilitated by the similarity of the crystal structures, specifically, peculiarity of fragments structure and method of their packing.

The structure of α -TCP consist of calcium and phosphate ions arranged in the two types of columns along the c axis, one contains only the calcium, other calcium and PO₄ tetrahedron [2]. Each calcium column is surrounded by six calcium-phosphate columns (Figure 5a).

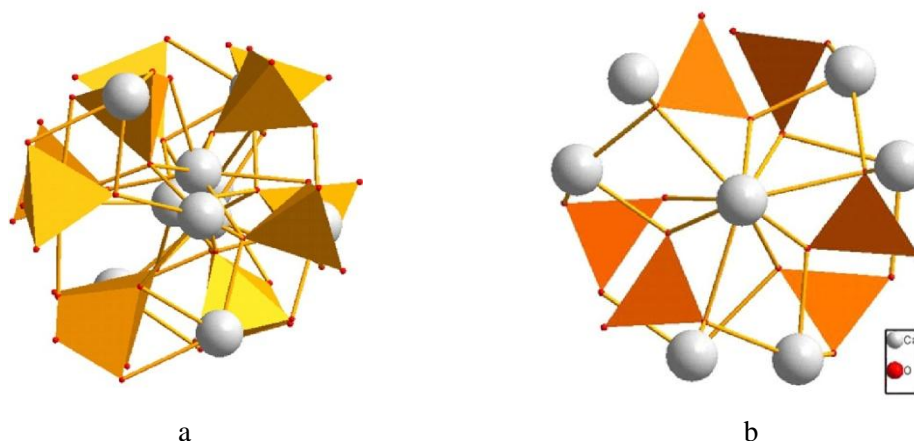


Figure 5. Fragment cluster of structure α -TCP (a) and apatite (b)

However, if these columns in α -TCP are distorted; forming their calcium atoms are generally displaced in a ab plane with respect to the axis c , the apatite lattice arrangement of calcium atoms is more regular (figure 5b). In the lattice of α -TCP, it is possible to select the cell (figure 1a) in which the columns are packaged in a manner characteristic for HA. In the process of α -TCP in HA transition one of the main features of the cation-anion columns of α -TCP, calcium deficiency, may be compensated by displacement of cations Ca^{2+} . The calcium located at the vertices of this cell displaced in the a, b directions (Figure 1a).

3. Conclusion

As a result of milling α -TCP powders in planetary mill in butanol the average particle diameter D decreases in 3.5 times (10 to 2.5 micrometers). According to the literature this reduction of the particle size produces a substantial decrease of the setting time and accelerates the hardening of the cement without significantly affecting the final strength. Relatively weak decrease of microblocks dimension (CSD) to ~ 80 nm, presumably explained by the specific processes of deformation of the particles in the liquid medium and the material of the vessel. The broadening of the X-ray reflections is determined mainly by decreasing of CSD. The contribution of dislocation type of plastic deformation is small. Synthesized after mechanical activation and subsequent annealing at 1300°C biphasic powders (HA + α -TCP) can be considered as two-component biomaterials with controlled solubility.

References

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