Microwave Sintering of Nano Size Powder β-TCP Bioceramics

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Abstract:
A nano sized beta tricalcium phosphate (β-TCP) powder was conventional sintered (CS) and microwave sintered (MW), in order to obtain dense β-TCP ceramics. In this work the effect of microwave sintering conditions on the microstructure, phase composition and mechanical properties of materials based on tricalcium phosphate (TCP) was investigated by SEM (scanning electron microscopy) and XRD (X-ray diffraction) and then compared with conventional sintered samples. Nano-size β-TCP powders with average grain size of 80 nm were prepared by the wet chemical precipitation method with calcium nitrate and di-ammonium hydrogen phosphate as calcium and phosphorus precursors, respectively. The precipitation process employed was also found to be suitable for the production of submicrometre β-TCP powder in situ. The β-TCP samples microwave (MW) sintered for 15 min at 1100°C, with average grain size of 3µm, showed better densification, higher density and certainly higher hardness than samples conventionally sintered for 2 h at the same temperature. By comparing sintered and MW sintered β-TCP samples, it was concluded that MW sintered β-TCP samples have superior mechanical properties.

Keywords: Synthesis nano powder β-TCP, Microwave sintering, SEM, XRD.

1. Introduction

Bioceramic materials are widely used to repair and reconstruct damaged parts of the human skeleton. Calcium phosphate ceramics materials based on hydroxyapatite (HAP) and tricalcium phosphate (TCP), due to their chemical composition, excellent biocompatibility, bioactivity and osteoconduction have received considerable attention as suitable bioceramics for the manufacture of osseous implants [1-6]. Dense forms of beta tricalcium phosphate with good mechanical properties are often used as reparation material in maxillofacial, dental and orthopaedic surgery [7]. The fracture toughness and strength of TCP is very low. Significant improvements have been made in increasing the fracture toughness of bioceramic materials through the control of density and microstructure, especially through the effect of grain size [7-8]. With decreasing grain size, the fraction of the grain boundary phase is increased and thereby a greater amount of energy is absorbed during crack propagation through the grain boundaries of such fine grained microstructures (nanostructures). The decrease in grain size from the micro to the nano level gives the explanation for the increased fracture toughness of dense bioceramic materials [9]. Nanostructured bioceramics are usually processed by compacting nanopowders at high pressures and sintering at different times and temperatures and in various atmospheres. Pressure assisted methods, such as hot pressing, hot isostatic pressing, sinter forging, etc., are also applied to obtain nanostructured ceramic materials [10-11].

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High sintering temperatures and long sintering times required for the consolidation of TCP powders often result in extreme grain coarsening which is characteristic for conventional sintering methods and results in the deterioration of the mechanical properties of TCP ceramics [12]. Hot pressing of bioceramics was found to allow the occurrence of densification at temperatures much lower than during conventional sintering. The advantages of the hot pressing technique are the enhancement of the densification kinetics and the limiting of grain growth, while the disadvantages are the limited geometry of the end product and the expensive equipment required. In order to overcome these problems, microwave sintering was found to show great potential in ceramics processing [13]. This technique provides a series of benefits, such as great microstructure control, no limit of the geometry of the product, improved mechanical properties of the materials and reduced manufacturing costs due to energy savings, lower temperatures of sintering and shorter processing times. Microwave heating is a fast sintering process fundamentally different from conventional radiant element techniques in that the energy can be addressed volumetrically throughout the material rather than relying on thermal conduction from the surface [14]. The aims of this work were the processing and characterization of dense nanostructured β-TCP ceramics, obtained by sintering and microwave of nano sized β-TCP powder, as well as comparing the microstructural and mechanical properties of dense materials obtained by these two methods. Effects of grain size on microhardness and indentation fracture toughness of β-TCP ceramic materials were also investigated.

2. Material and methods

2.1. Powder synthesis

β-TCP nanopowders were synthesized by the reaction of calcium nitrate tetra-hydrate (Ca(NO₃)₂·4H₂O, 98%, Merck) with diammonium hydrogen phosphate ((NH₄)₂HPO₄, 99%, Merck). Briefly, 500 mL of 0.4 mol (NH₄)₂HPO₄ solution with pH = 4 was vigorously stirred at room temperature, and 500 mL of 0.6 mol Ca(NO₃)₂ with pH = 7.3 was added drop wise over 150–200 min to produce a white precipitate. Throughout the mixing process the pH of the system was maintained at pH = 8 by adding of 0.1 M sodium hydroxide (NaOH, 99%, Merck). The obtained white suspension was then stirred for 12 h. The synthesized precipitate was washing with distilled water and then with 100% ethanol to improve the dispersion characteristics. The suspension was filtered in a filter glass with application of mild suction. After filtration the compact, sticky filter cake, was dried at 80°C for 24 h. The as-dried powders were crushed by using mortar and pestle and calcined in alumina crucible at 700°C for 2 h. The β-TCP powders were uniaxially pressed at 100 MPa using a stainless steel mold. The pressed disc green compacts, 12 mm in diameter, were sintered in an electrical furnace by heating to the desired temperature, 900°C, 1000°C and 1100°C, at a heating rate of 20°C/min and maintaining the temperature for 2 h. In all cases, the disc samples were placed at the same location in the microwave furnace by heating at 900°C, 1000°C and 1100°C for 15 min. The density of the green samples was obtained by measuring the dimensions and weight, and that of sintered samples by the Archimedes method.

2.2. X-ray diffraction (XRD) and microscopic examinations

Evaluation of crystalline phases was investigated by X-ray diffractometer (Siemens, model D-500) using CuKα radiation. Silicon powder was used as the standard material for semi-quantitative analysis of precipitated phases. The mean crystallite size (D) was calculated from the XRD line broadening measurement from the Scherrer equation [31]:

\[ D = \frac{0.89\lambda}{\beta \cos \theta} \]  
(1)
Where $\lambda$ is the wavelength of the used Cu K\textalpha radiation, $\beta$ is the full width at the half maximum of the $\beta$-TCP line and $\theta$ is the diffraction angle. The Ca/P ratio of the dried powder was measured by inductively coupled plasma (ICP) atomic emission spectroscopy (model Varian). The morphology of the microwave and conventionally sintered samples was observed by a scanning electron microscope (SEM VEGA-TESCAN).

3. Results and discussion

The Ca/P ratio of the $\beta$-TCP powder, as determined by ICP analyses, was $1.51\pm 0.01$. The SEM micrograph of the obtained $\beta$-TCP powder is shown in fig. 1.

![SEM micrograph of $\beta$-TCP powder](image)

**Fig. 1.** SEM photomicrographs of as-prepared $\beta$-TCP nanopowders.

The XRD analysis was performed using the X-ray diffractometer. The straight base line and sharp peaks of the diffractogram in fig. 2 confirmed that the products were well crystallized. The results revealed that the as-prepared powder was composed of highly crystalline and no second phase other than $\beta$-TCP. The average crystallite size is determined by Scherrer equation, of this sample 80 nm.

![XRD pattern of $\beta$-TCP](image)

**Fig. 2.** XRD patterns of $\beta$-TCP powders.

The SEM micrograph of the green compact isostatically pressed at 100 MPa is shown in fig. 3. The compact, as can be clearly seen, was uniform, as the result of applied high isostatic pressure and the presence of soft aggregates in the starting $\beta$-TCP powder. The green
compact density was 1.94 g/cm³, or 63% of the theoretical density. Green compacts of β-TCP were sintered in air to obtain compacts having a dense microstructure.

Fig. 3. Typical SEM micrograph of a green compact of β-TCP powder pressed at 100 MPa.

The SEM micrograph of the sample obtained by sintering at 900°C for 2 h is shown in fig. 4. The fig. shows that this compact has a porous microstructure with mean grain size of 0.5µm.

Fig. 4. SEM micrograph of a β-TCP sample conventional sintered at 900°C.

SEM micrographs of samples sintered at 1000°C and 1100°C for 2 h are shown in fig.s 5–6, respectively. The sample sintered at 900°C for 2h had a high porosity, which decreased with increasing sintering temperature. On sintering in air at 1000°C and 1100°C, the β-TCP compacts increased in grain size from 2µm to 4µm. The SEM micrographs shown that conventional sintered samples were porous and that the microstructures were non-uniform.
Fig. 5. SEM micrograph of a \( \beta \)-TCP sample conventional sintered at 1000\(^\circ\)C.

Fig. 6. SEM micrograph of a \( \beta \)-TCP sample conventional sintered at 1100\(^\circ\)C.

Fig. 7. XRD patterns of pure \( \beta \)-TCP bioceramics, MW sintered at 900\(^\circ\)C, 1000\(^\circ\)C and 1100\(^\circ\)C for 15 min.
The XRD patterns of the ų-TCP samples MW sintered at 900°C, 1000°C and 1100°C for 15 min, shown in fig. 7, exhibited just peaks of ų-TCP crystalline phase.

The SEM micrographs of surface of the ų-TCP samples MW sintered at 900°C, 1000°C and 1100°C for 15 min, presented in figs 8–10, showed dense and uniform grained microstructures. The mean grain size increased from nano to microlevel with increasing of temperature from 900°C to 1100°C. The mean grain size of the sample MW sintered at 900°C was 150 nm and on increasing of the temperature to1100°C, the grain size increased to 3µm. The relative density of the ų-TCP samples MW sintered at 900–1100°C are shown in fig. 11. During the processing of ų-TCP ceramics at 900°C and 1000°C, density of the samples was 72% and 82%. With increasing of the temperature from 1000°C to 1100°C, the density of the samples insignificantly increased. The relative density of sample sintered at 1100°C by sintering and MW is 81% and 98% respectively. The result confirmed by SEM image in figs 6 and 10. The samples obtained by conventional sintering had an around 17% smaller density
than the MW sintered samples. By comparing the results of microwave and conventional sintering $\beta$-TCP it can be concluded that calcium phosphate ceramics, such as HAP and HAP/TCP, are microwave sensitive. More dense and uniform fine grained materials were obtained at 1000°C and 1100°C by MW sintering with an eight times shorter holding time.

Fig. 10. SEM micrograph of a $\beta$-TCP sample MW sintered at 1100°C.

Fig. 11. Relative density of conventional sintered and MW sintered at different temperatures.

Fig. 12. Microhardness of conventional sintered and MW sintered at different temperatures.
These results confirmed that the employment of microwaves during the sintering of nanosized β-TCP powders had a positive effect on the densification and microstructural characteristics of β-TCP due to the homogenous microwave energy distribution, which leads to a volumetrically uniform heating. The hardness of the conventional and MW sintered β-TCP bioceramics as a function of temperature are shown in Fig. 12. The increase of sintering temperature from 900°C to 1100°C led to an increase in the hardness from 189HV to 310HV for CS and 250 to 420 for MW. The sample MW sintered at 1100°C had the maximum value of hardness.

4. Conclusion

Fine grain sized pure β-TCP biomaterials were processed by microwave sintering, starting from stoichiometric and calcium deficient nano sized β-TCP powders. The microstructures of the monophase β-TCP samples microwave sintered for 15 min in the range of temperature 900–1100°C were dense and uniform, with a mean grain size in the range from 150 nm to 3.0µm. Microwave sintering makes bioceramic samples possible to enhance densification kinetics and limit grain growth.

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5. References

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Садржај: Са циљем да се постигне густа β-TCP керамика, нано честице бета трикалцијум фосфата (β-TCP) синтезоване су конвенционалним методом (КС) и микроталасно (МС). У овом раду ефекти услова микроталасног синтеза на микроструктуру, фазни састав и механичка својства материјала на бази трикалцијума фосфата испитани су СЕМ и рентгенском дифракцијом и онда су резултати упоређивани са резултатима добијеним конвенционалном методом синтеза. Нано честице β-TCP праха са просечном величином зrna од 80 нм преипремљене су мокром хемијском методом преципитације калцијума нитрата и диамногидроген фосфата са кalicijум и фосфорним прекурсорима. Употребљени процес преципитације је такође погодан за добијање субмикрометарског β-TCP праха in situ. β-TCP узорци синтезован микроаласно 15 минута на 1100˚C, са просечном димензијом зrna од 3µm, показују боњу денсификацију, већу густину и наравно већу тврдоћу од узорака синтезованих конвенционално 2 h на истој температури. Поредећи узорке добијене након две врсте синтеза, закључено је да узорци синтезован микроаласно имају боља механичка својства.
Кључне речи: синтеза нано праха β-TCP, микроталасно синтеза, СЕМ, рентгенска дифракција