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Microwave sintering of fine grained HAP and HAP/TCP bioceramics

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Abstract

The effect of microwave sintering conditions on the microstructure, phase composition and mechanical properties of materials based on hydroxyapatite (HAP) and tricalcium phosphate (TCP) was investigated. Fine grained monophase HAP and biphasic HAP/TCP biomaterials were processed starting from stoichiometric and calcium deficient nanosized HAP powders. The HAP samples microwave (MW) sintered for 15 min at 900 °C, with average grain size of 130 nm, showed better densification, higher density and certainly higher hardness and fracture toughness than samples conventionally sintered for 2 h at the same temperature. By comparing MW sintered HAP and HAP/TCP samples, it was concluded that pure HAP ceramics have superior mechanical properties. For monophase MW sintered HAP samples, the decrease in the grain size from 1.59 μm to 130 nm led to an increase in the fracture toughness from 0.85 MPa $m^{1/2}$ to 1.3 MPa $m^{1/2}$.

Keywords: B. Grain size; C. Hardness; D. Apatite; Microwave sintering; Toughness

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1. Introduction

Biomaterials are now defined as ‘‘natural or synthetic materials suitable for introduction into living tissue, especially as part of a medical device’’ [1]. 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 [2,3]. Granular, dense or controlled porous forms of such phosphate ceramics, prepared through conventional methods, are generally available in clinical practice.

Dense forms of hydroxyapatite with good mechanical properties are often used as reparation material in maxillofacial, dental and orthopaedic surgery. Dense HAP in tooth form has been used as an immediate tooth root replacement to minimize alveolar ridge resorption, which follows tooth loss, and to maintain ridge width and height. In particulate form, dense hydroxyapatite is used as filler in bony defects and as a filler association for the placement of metal implants [4,5].

Even though the bioactivity and biocompatibility of HAP and TCP are excellent, their brittle nature and low fracture toughness and hardness, especially in wet environments as would be found under physiological conditions, limits the use of this material in load-bearing clinical application [6]. The fracture toughness is very low in a brittle ceramic material, such as HAP and TCP. 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. 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 nanolevel gives the explanation for the increased fracture toughness of dense bioceramic materials [7–10].

Dense nanostructured bioceramic materials are usually obtained by pressing and conventional sintering of nanopowders using pressure assisted methods, such as hot pressing, hot isostatic pressing, sinter forging, etc. [11–13]. The high sintering temperatures and long sintering times required for the consolidation of HAP powders often result in extreme grain

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coarsening and decomposition of the HAP, which is characteristic for conventional sintering methods and results in the deterioration of the mechanical properties of HAP ceramics [14,15]. Hot pressing of hydroxyapatite was found to allow the occurrence of densification at temperatures much lower than during conventional sintering [16,17]. 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 [18]. 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.

During the last decade, microwave sintering of ceramic materials has been widely investigated by various researchers. Microwave sintering of calcium hydroxyapatite was first reported by Fang et al. [19–21]. 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 [22,23]. Conventional furnaces heat samples by the surface heating mechanism and, depending on the rate of heating, a large thermal gradient from the surface to the centre can be generated within a sample, particularly with materials heaving a poor thermal conductivity. However, volumetric heating *via* microwave radiation ensures uniform heating and almost no thermal gradient, which allows higher heating rates and reduces the processing time.

The aim of this study was to investigate the processing of fine grained pure hydroxyapatite and biphasic HAP/TCP bioceramics by microwave sintering, starting from stoichiometric and calcium deficient nanosized HAP powders, obtained by two modified chemical precipitation syntheses. The effects of the microwave sintering conditions on the microstructure, phase composition and mechanical properties of the obtained materials based on HAP and TCP were investigated. The main reason for using the microwave sintering technique in this study was to obtain uniform fine grained bioceramic materials with good mechanical properties by reducing the temperature and the time of sintering. The influence of microstructure and phase composition on the fracture toughness and hardness of microwave sintered HAP and HAP/TCP bioceramics was also investigated. The results obtained by microwave sintering were compared with those obtained by conventional sintering methods.

2. Experimental

The starting calcium hydroxyapatite powders were obtained using two modified precipitation syntheses. In order to process monophasic HAP bioceramic materials, stoichiometric nanosized hydroxyapatite, HAP1, powder was obtained by a precipitation method described earlier [17,24–26]. As the first step in the processing of biphasic HAP/TCP bioceramics, calcium deficient calcium hydroxyapatite, HAP2, was obtained according to another previously described precipitation method [13,15,27]. The particle size distribution was determined from water dispersions using a laser particle size analyzer, Mastersizer 2000 Malvern Instruments Ltd., UK.

The HAP1 and HAP2 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 automated microwave laboratory furnace (Linn High Therm MHTD 1800-4,8/2,45-135) by heating to the desired temperature, 900 °C, 1000 °C, 1100 °C and 1200 °C, at a heating rate of 20 °C/min and maintaining the temperature for 15 min. The sample temperature was monitored continuously with an optical pyrometer at the top of the furnace. In all cases, the disc samples were placed at the same location in the microwave furnace, in order to avoid the influence of geometric factor. For comparison, the same green compacts were conventionally sintered at 900 °C and 1000 °C for 2 h.

The morphology of the microwave and conventionally sintered samples was observed by a scanning electron microscope (SEM), Jeol JSM 5800, operated at 20 keV. The average grain size of the samples was determined by image analysis of the SEM micrographs (Image Pro Plus Program, version 4.0 for Windows). More than 100 HAP grains were counted to obtain an average value. The density of the green samples was obtained by measuring the dimensions and weight, and that of sintered samples by the Archimedes method.

X-ray diffraction patterns of the HAP powders and sintered compacts were recorded using a Bruker D8 advance diffractometer, in the 2θ ranging from 20° to 50° with a scan step of 0.02°.

The microwave and conventionally sintered compacts were tested for hardness and indentation fracture toughness. The hardness of the polished HAP and HAP/TCP compacts was measured with a Buehler Indentament 1100 series, Vickers Indentation Hardness Tester. The K_{ic} values were calculated using the following formula which was derived from the model proposed by Evans and Charles [28]: $K_{\mathrm{ic}} = 0.0824\,Pc^{-3/2}$ where P is the indentation load and c the length of the induced radial crack.

3. Results and discussion

The Ca/P ratio of the HAP1 powder was 1.67 ± 0.01 [17], which shows that stoichiometric hydroxyapatite was obtained using the first modified precipitation synthesis. The Ca/P ratio 1.62 ± 0.01 of the HAP2 powder shows that calcium deficient hydroxyapatite was obtained in the second precipitation synthesis [15]. The XRD patterns of the HAP1 and HAP2 powders exhibited peaks corresponding to the calcium hydroxyapatite phase [15].

The crystallite size of the HAP powders, calculated by the Scherrer equation, was around 35 nm. The TEM micrographs [15] of the powders revealed elongated rod-like particles of size between 50 nm and 150 nm. The HAP1 and HAP2 powders appeared agglomerated consisting of a large numbers of fine HAP particles [13,17].

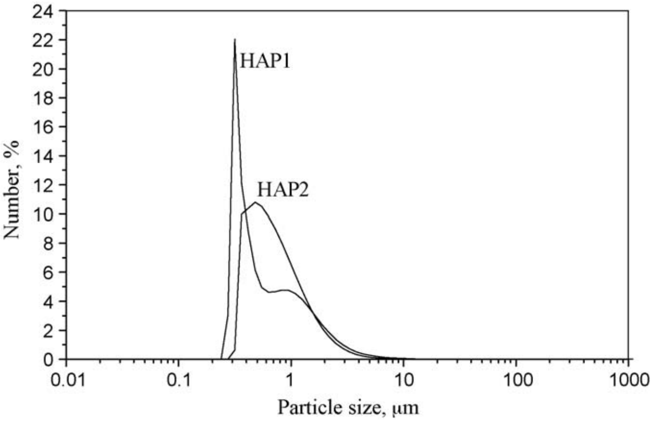

Fig. 1. Particle size distribution of the agglomerated HAP1 and HAP2 powders.

The particle size distribution of the agglomerated HAP1 and HAP2 powders are shown in Fig. 1. The diagrams confirmed that the nanosized HAP powders were agglomerated and that the agglomerate sizes were in the range from approximately 200 nm to few microns. The density of the uniaxially pressed green compacts was about 1.35 g/cm^3, or 44% of the theoretical density.

The XRD patterns of the HAP1 samples MW sintered at 900 °C, 1000 °C, 1100 °C and 1200 °C, shown in Fig. 2, exhibited peaks suggesting that HAP was the prevailing crystalline phase.

The XRD patterns of the HAP2 samples sintered at 900 °C, 1000 °C, 1100 °C and 1200 °C, presented in Fig. 3, showed that MW sintering of the calcium deficient HAP2, resulted in biphasic HAP/TCP bioceramic materials. The HAP2 samples sintered at 900 °C and 1000 °C were biphasic mixtures of HAP and β-TCP. By comparing the phase compositions of the HAP2 samples, sintered at 900 °C and 1000 °C, with those of the HAP2 samples sintered at 1100 °C and 1200 °C, it can be concluded that a phase transformation β-TCP into α-TCP occurred when the temperature of MW sintering was higher than 1100 °C.

The SEM micrographs of fracture sections of the HAP1 samples MW sintered at 900 °C, 1000 °C, 1100 °C and 1200 °C for 15 min, presented in Figs. 4–7, showed dense and uniform grained microstructures. The mean grain size increased from nano to microlevel with increasing of temperature from 900 °C to 1200 °C. The mean grain size of the sample MW sintered at 900 °C was 130 nm and on increasing of the temperature to 1200 °C, the grain size increased to 1.59 μm.

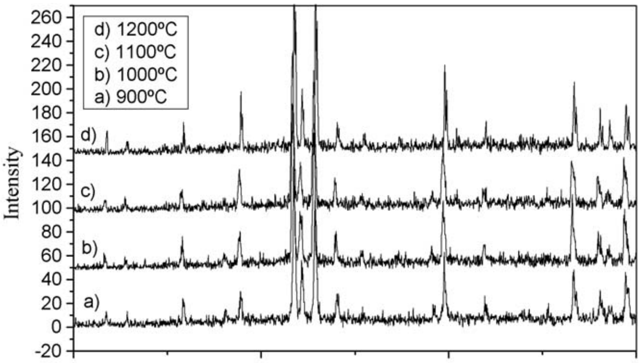

Fig. 2. XRD patterns of pure HAP bioceramics, MW sintered at 900 °C, 1000 °C, 1100 °C and 1200 °C.

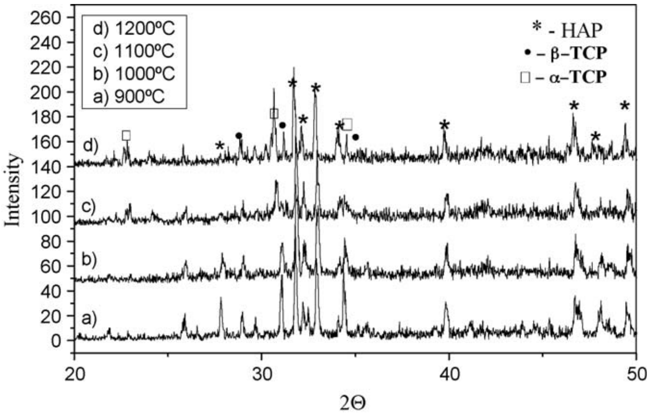

Fig. 3. XRD patterns of biphasic HAP/TCP bioceramics, MW sintered at 900 °C, 1000 °C, 1100 °C and 1200 °C.

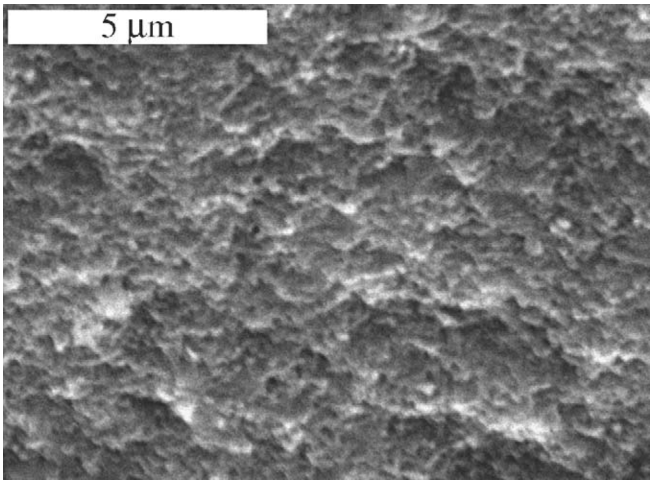

Fig. 4. SEM micrograph of a HAP1 sample MW sintered at 900 °C.

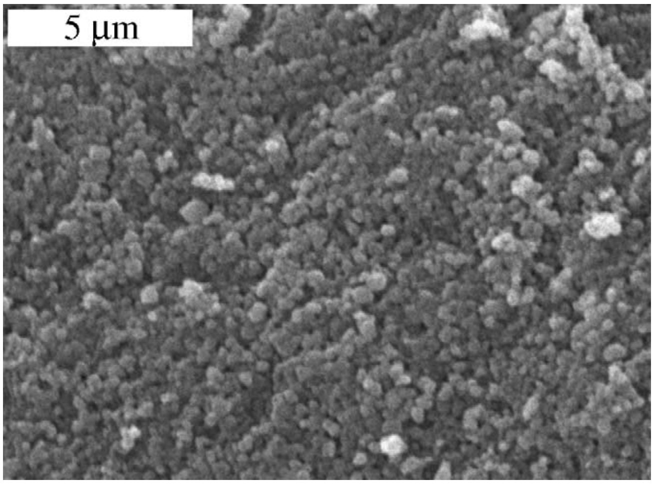

Fig. 5. SEM micrograph of a HAP1 sample MW sintered at 1000 °C.

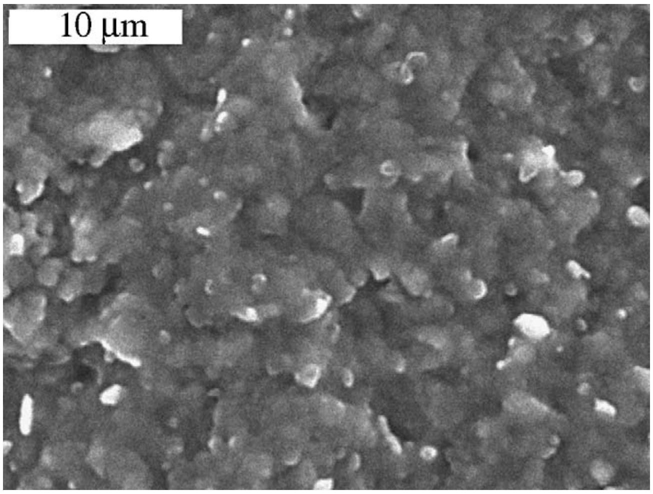

Fig. 6. SEM micrograph of a HAP1 sample MW sintered at 1100 °C.

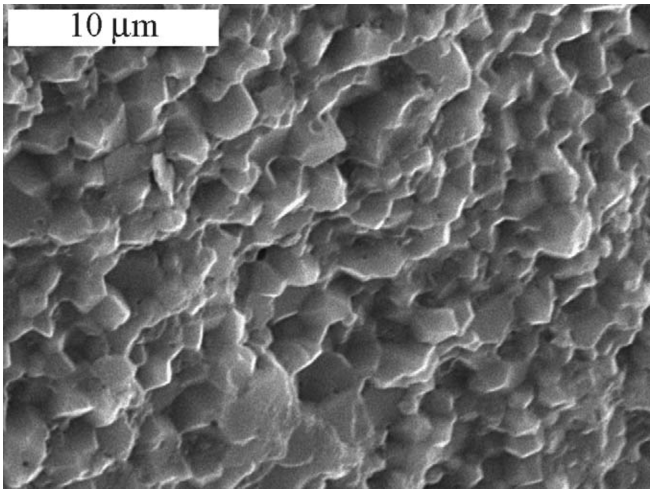

Fig. 7. SEM micrograph of a HAP1 sample MW sintered at 1200 °C.

The SEM micrographs of fracture sections of the HAP2 samples MW sintered at 900 °C, 1000 °C, 1100 °C and 1200 °C for 15 min are presented in Figs. 8–11. The mean grain size of the HAP2 samples sintered at 900 °C and 1000 °C were 100 nm and 480 nm, respectively (Figs. 8 and 9.). At temperatures higher than 1000 °C, the grain size of HAP2 compacts rapidly increased. On increasing the sintering temperature to 1200 °C, grain size increased to 4.70 μm.

The linear shrinkage of the HAP1 and HAP2 samples MW sintered at 900–1200 °C are shown in Fig. 12. During the processing of HAP1 ceramics at 900 °C and 1000 °C, linear shrinkage of the samples was 20.4% and 24.5%. With increasing of the temperature from 1000 °C to 1200 °C, the shrinkage of the samples insignificantly increased, but the grain size rapidly increased, from the nano to the microlevel, from 240 nm to 1.59 μm (Fig. 13). The densities of the HAP1 ceramics sintered at 900–1200 °C were in the range of 2.76–2.98 g/cm^3.

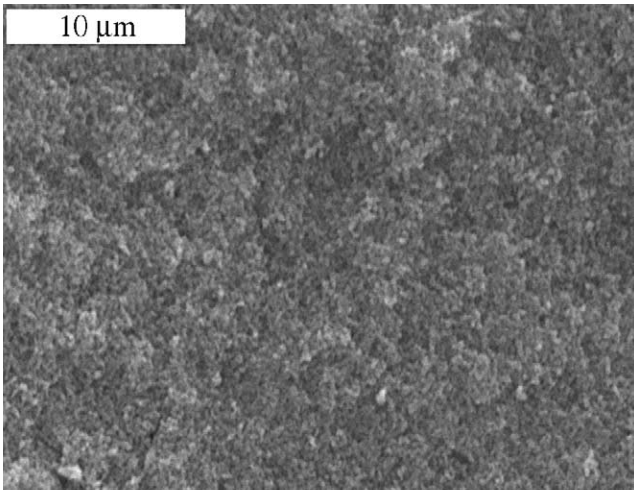

Fig. 8. SEM micrograph of a HAP2 sample MW sintered at 900 °C.

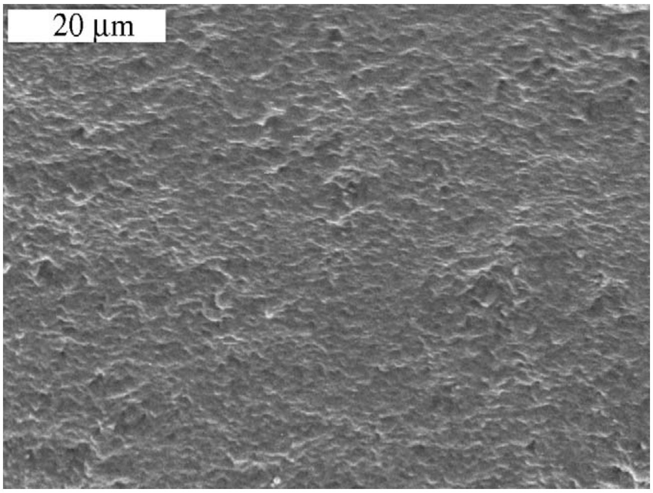

Fig. 9. SEM micrograph of a HAP2 sample MW sintered at 1000 °C.

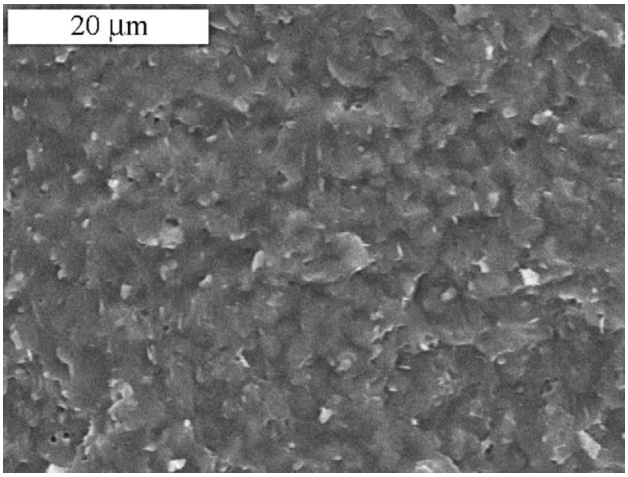

Fig. 10. SEM micrograph of a HAP2 sample MW sintered at 1100 °C.

During the formation of the biphasic HAP2 ceramics by MW sintering, the dependence of the linear shrinkage on temperature was different than during the sintering of the stoichiometric HAP1 (Fig. 12). After the sintering at 900 °C, the linear shrinkage of the pellet was very small, around 11%, and the density of this sample was 1.60 g/cm^3. These results confirmed the lower sinterability at 900 °C of the HAP2 powder

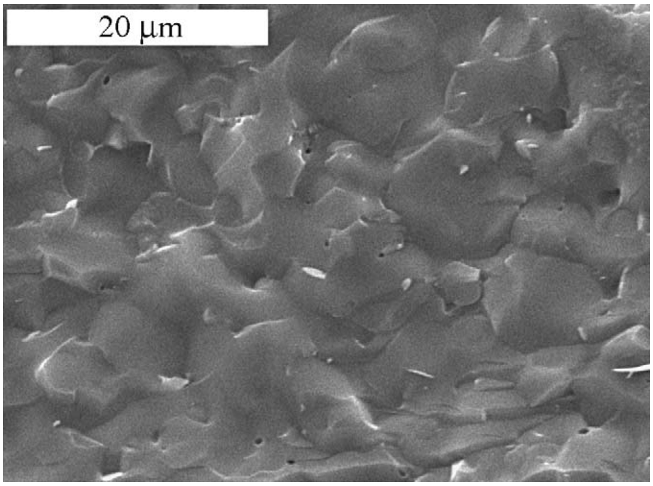

Fig. 11. SEM micrograph of a HAP2 sample MW sintered at 1200 °C.

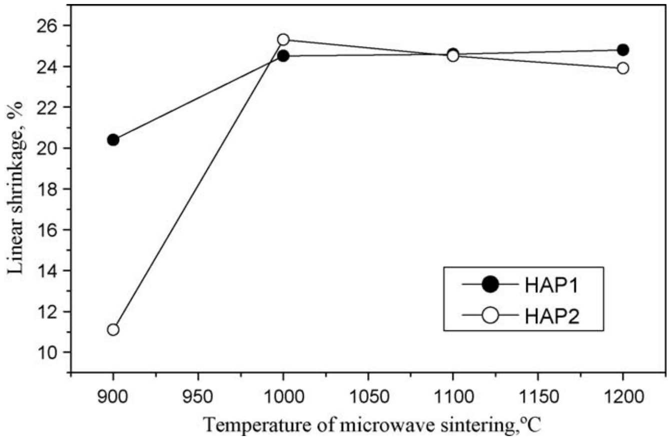

Fig. 12. Linear shrinkage of the HAP1 and HAP2 samples MW sintered at different temperatures.

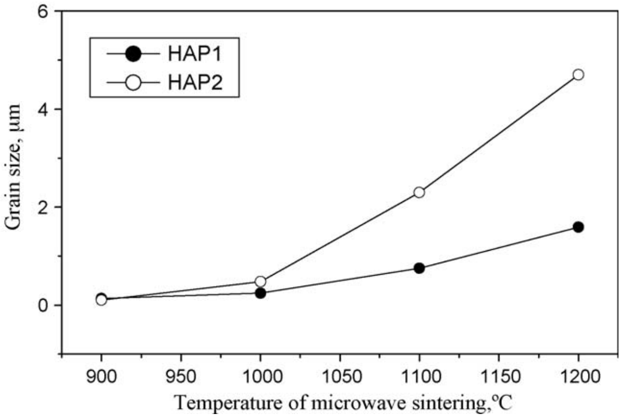

Fig. 13. The grain size of the HAP1 and HAP2 samples as a function of the MW sintering temperature.

in comparison with the stoichiometric HAP1 powder. The maximum value of the linear shrinkage during MW sintering of the HAP2 powder was at 1000 °C and on increasing the sintering temperature above this value, the linear shrinkage slightly decreased. The phase transformation β-TCP → α-TCP at temperatures higher than 1100 °C can be the main reason for a small expansion and the decrease of the linear shrinkage. With increasing the temperature from 900 °C to 1200 °C, the grain size of the HAP/TCP bioceramics increased more rapidly, from 100 nm to 4.7 μm, than during the formation of the pure HAP bioceramics (Fig. 13.). This greater increase in the grain size during the sintering of the calcium deficient HAP than the stoichiometric HAP agrees with other published results [29]. The coalescence of the HAP particles occurs in three successive steps, a rounding of particles, the formation of necks at the contacts of the particles and coalescence of these particles at a rate that appears to increase as the Ca/P ratio of the initial powder decreases. The increase of the grain size with decreasing Ca/P ratio of the initial powder must relate to the strong particle coalescence that occurs at the low temperature in the calcium deficient HAP powder compact before the formation of the biphasic mixture [29]. The density of the biphasic HAP sample resulting from MW sintering at 1000 °C was 2.60 g/cm^3, and on increasing the temperature from 1000 °C to 1200 °C, the density slightly decreased to 2.56 g/cm^3 due to phase transformation from β-TCP to α-TCP.

The microstructures of the fracture surfaces of the HAP1 and HAP2 samples obtained by conventional sintering at 900 °C and 1000 °C for 2 h are presented in Figs. 14–17. The SEM micrographs shown that conventional sintered samples were porous and that the microstructures were non-uniform. The samples obtained by conventional sintering had an around 2% smaller linear shrinkage than the MW sintered samples.

By comparing the results of microwave and conventional sintering of the stoichiometric and calcium deficient hydroxyapatite, it can be concluded that calcium phosphate ceramics, such as HAP and HAP/TCP used in present study, are microwave sensitive. More dense and uniform fine grained materials were obtained at 900 °C and 1000 °C by MW sintering with an eight times shorter holding time. These results confirmed that the employment of microwaves during the sintering of nanosized HAP powders had a positive effect on the densification and microstructural characteristics of HAP-based

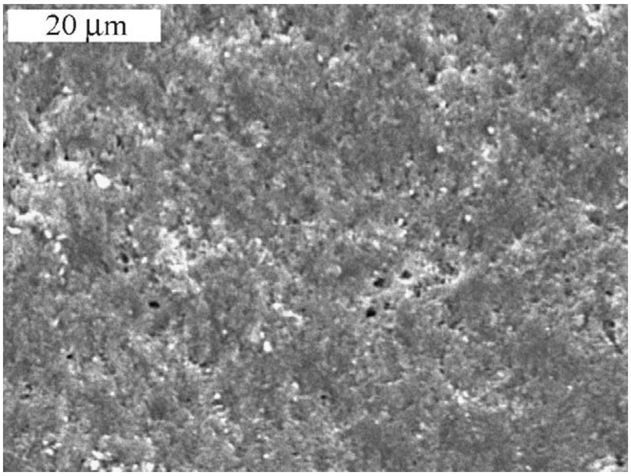

Fig. 14. SEM micrograph of an HAP1 sample conventionally sintered at 900 °C.

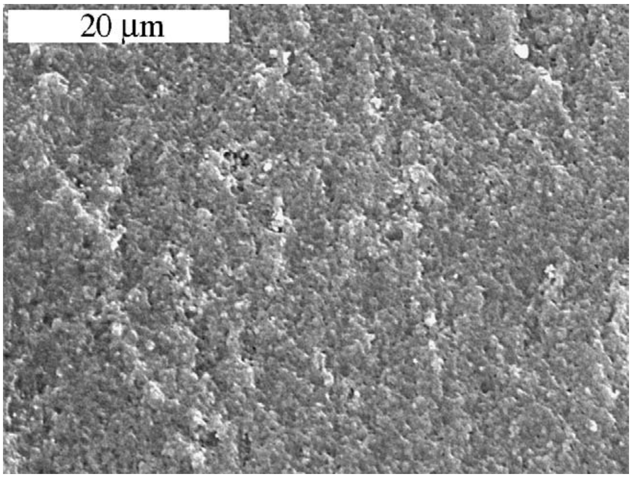

Fig. 15. SEM micrograph of an HAP2 sample conventionally sintered at 900 °C.

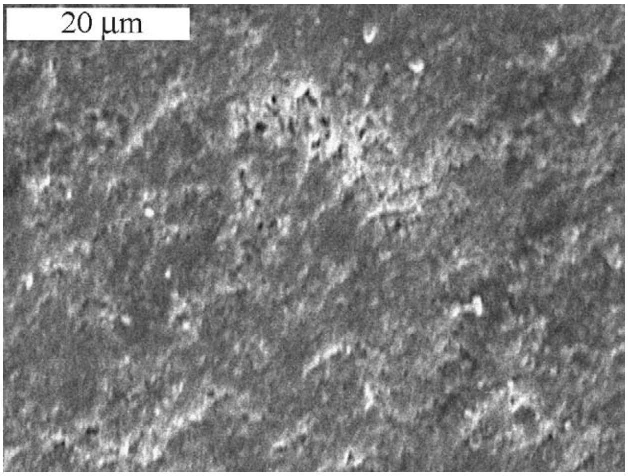

Fig. 16. SEM micrograph of an HAP1 sample conventionally sintered at 1000 °C.

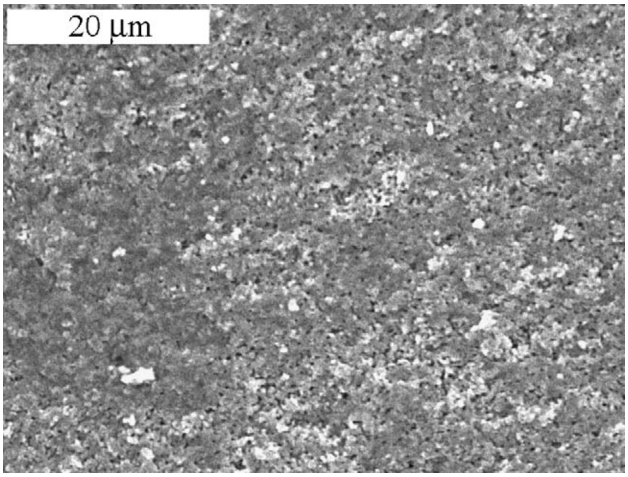

Fig. 17. SEM micrograph of an HAP2 sample conventionally sintered at 1000 °C.

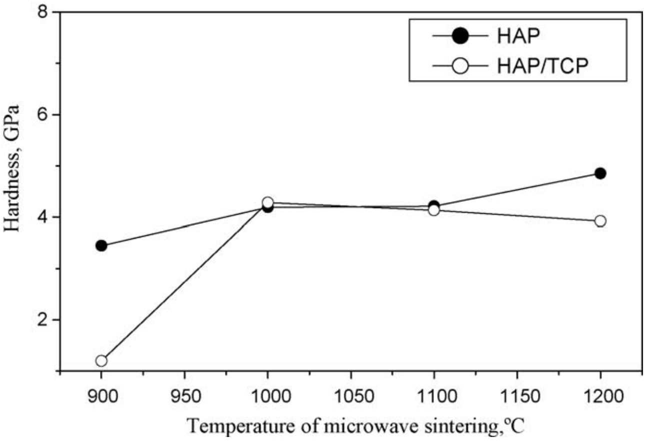

Fig. 18. The hardness of the HAP and HAP/TCP bioceramic materials as a function of the MW sintering temperature.

bioceramics due to the homogenous microwave energy distribution, which leads to a volumetrically uniform heating.

The hardness of the MW sintered HAP and HAP/TCP bioceramics as a function of temperature are shown in Fig. 18. For pure HAP samples, the increase of sintering temperature from 900 °C to 1200 °C led to an increase in the hardness from 3.45 GPa to 4.85 GPa. Of the biphasic HAP/TCP bioceramic, the sample MW sintered at 1000 °C had the maximum value of hardness 4.28 GPa. On increasing the temperature from 1000 °C to 1200 °C, the hardness of HAP/TCP bioceramics decreased due to the transformation of β-TCP into α-TCP. This phase transformation induced residual stresses within the densified material and this could be the reason for the slightly decreased hardness of the HAP/TCP bioceramics.

The fracture toughness of the processed bioceramics is shown in Fig. 19 as a function of MW sintering temperature. The fracture toughness of the HAP/β-TCP compact sintered at 900 °C was 0.56 MPa $m^{1/2}$ and increasing the temperature to 1000 °C led to an increase of the fracture toughness to 0.75 MPa $m^{1/2}$. The increasing of fracture toughness agrees with the rapid increase of the linear shrinkage and density of the HAP/β-TCP compacts. With increasing sintering temperature

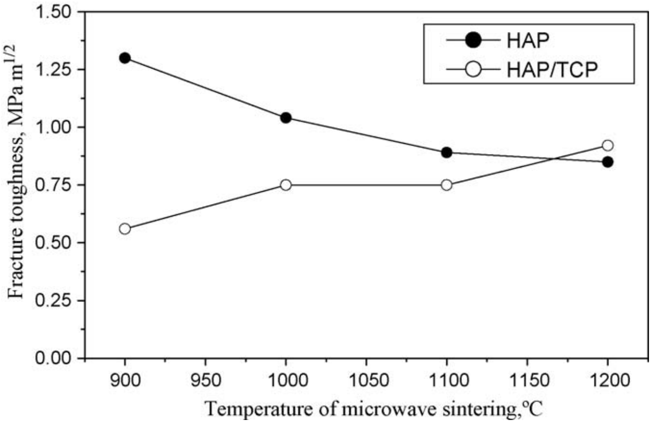

Fig. 19. The fracture toughness of the HAP and HAP/TCP bioceramic materials as a function of the MW sintering temperature.

to 1200 °C, β-TCP in particular transformed into α-TCP and the fracture toughness of the HAP/TCP compacts increased to 0.92 MPa $m^{1/2}$. The reason for this increase of the fracture toughness of the HAP/TCP ceramics can be the higher densification, despite the small decrease of the density, as a consequence of the transformation of β-TCP into α-TCP. The decrease of the density at temperatures higher than 1000 °C was due to the noticeably lower density of α-TCP (2.84 g/cm^3) compared to that of β-TCP (3.07 g/cm^3). The second reason for the increase of fracture toughness of the HAP/TCP ceramics with increasing sintering temperature could be an extensive phase transformation from HAP to TCP and the presence of a higher amount of TCP in the sintered samples (K_{ic} (HAP) = 0.9 MPa $m^{1/2}$ and K_{ic} (TCP) = 1.3 MPa $m^{1/2}$) [1].

Despite TCP having a higher theoretical fracture toughness than HAP, the presence of α- and β-TCP is highly detrimental to the sintering and mechanical properties of the final HAP/TCP bioceramics [29–31]. The sintering is retarded when the content of TCP in the biphasic mixture increases. The presence of TCP in the HAP matrix is a limiting factor for sintering, which could be linked to diffusion phenomena and to particle coalescence that occurs at a lower temperature [29]. The predominant influence of the formation of TCP phase on the mechanical and nanomechanical properties of HAP/TCP ceramics was also confirmed in a previous paper [15]. In that research the higher standard deviation of the nanomechanical properties of the HAP/TCP samples than the monophase HAP samples also reflected the inhomogeneous properties due to the formation of the second phase. For fine grained materials, the mechanical properties are better for pure HAP ceramics than for HAP/TCP ones, confirming the prevailing effect of the β-TCP phase on the mechanical properties. In order to avoid diminishment of the mechanical properties, the absence of the α- and β-TCP in HAP bioceramics is advisable.

By analyzing Fig. 19 it can be concluded that noticeably higher values of the fracture toughness were obtained for the monophase HAP samples than for the HAP/TCP samples. The fracture toughness of pure HAP and HAP/TCP compacts sintered at 900 °C were 1.30 MPa $m^{1/2}$ and 0.56 MPa $m^{1/2}$, respectively, and for the compacts obtained at 1100 °C, 0.89 MPa $m^{1/2}$ and 0.75 MPa $m^{1/2}$, respectively. A decreasing of the MW sintering temperature and a decreasing grain size at the nanolevel yields an increase in the difference of the fracture toughness values between the HAP and HAP/TCP biomaterials. The fracture toughness of the monophase HAP samples increased with decreasing sintering temperature, which confirmed that the grain size has the dominant effect on the fracture toughness of monophase HAP bioceramics (Fig. 20.). Previously, it was seen that the fracture toughness of HAP/TCP ceramics increased with the increasing sintering temperature due to the higher densification at higher temperatures and the presence of an increased amount of TCP. A low amount of TCP phase would act as a limiting agent of the sintering of HAP by hindering diffusion on account of the decrease of the densification of the material. Due to the detrimental effect of β-TCP on the sintering of HAP, a definitely lower densification was realised at 900 °C during the formation of the HAP/TCP samples, and this is the main reason for the noticeably higher fracture toughness of the monophase fine grained HAP sample obtained at 900 °C.

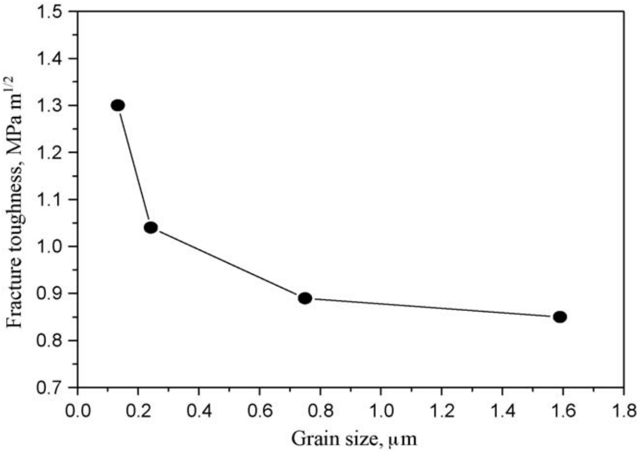

Fig. 20. The fracture toughness of pure HAP bioceramic materials as a function of grain size.

For the MW sintered pure HAP compacts, a decrease of the sintering temperature from 1200 °C to 900 °C led to an increase in the fracture toughness from 0.85 MPa $m^{1/2}$ to 1.3 MPa $m^{1/2}$ (Fig. 19.). The fracture toughness of the pure HAP bioceramics as a function of grain size is shown in Fig. 20. The HAP compacts MW sintered at 1100 °C and 1200 °C for 15 min had mean grain sizes of 750 nm and 1.59 μm, respectively, while the values of the fracture toughness were 0.89 MPa $m^{1/2}$ and 0.85 MPa $m^{1/2}$, respectively. A decreasing of the grain size to 240 nm resulted in an increase of the fracture toughness to 1.04 MPa $m^{1/2}$, while the maximum value of the fracture toughness, 1.30 MPa $m^{1/2}$, was attained for the sample with lowest mean grain size of 130 nm. In general, the values of the fracture toughness for most HAP samples reported in the literature varied between 0.60 to about 1 MPa $m^{1/2}$ [7,21,31,32]. Raynaud et al. [31] measured a fracture toughness of 1.0 ± 0.1 MPa $m^{1/2}$ for a hot pressed HAP-based bioceramics. Banerjee et al. [32] obtained dense HAP bioceramics using conventional sintering, which exhibited fracture toughness values ranging from 0.6 to 1.0 MPa $m^{1/2}$.

The type of fracture in microstructured HAP ceramics obtained at high temperatures during long sintering times is usually found to be transgranular [9,17,33,34]. An increase of fracture toughness with decreasing grain size is usually observed in ceramics when the fracture mechanism is intergranular because the major contribution to crack resistance is related to the passage of the cracks through the grain boundaries. The fracture mechanism of microwave sintered pure HAP samples in this study was intergranular, as confirmed by the SEM micrographs of the fracture surface shown in Figs. 4–7, in which grains pulled out from the structure are observed. The reduction of the temperature and time using microwave sintering led to a decrease of the grain size and to an increase of energy absorption during crack propagation through the grain boundaries. This gives the explanation for the higher

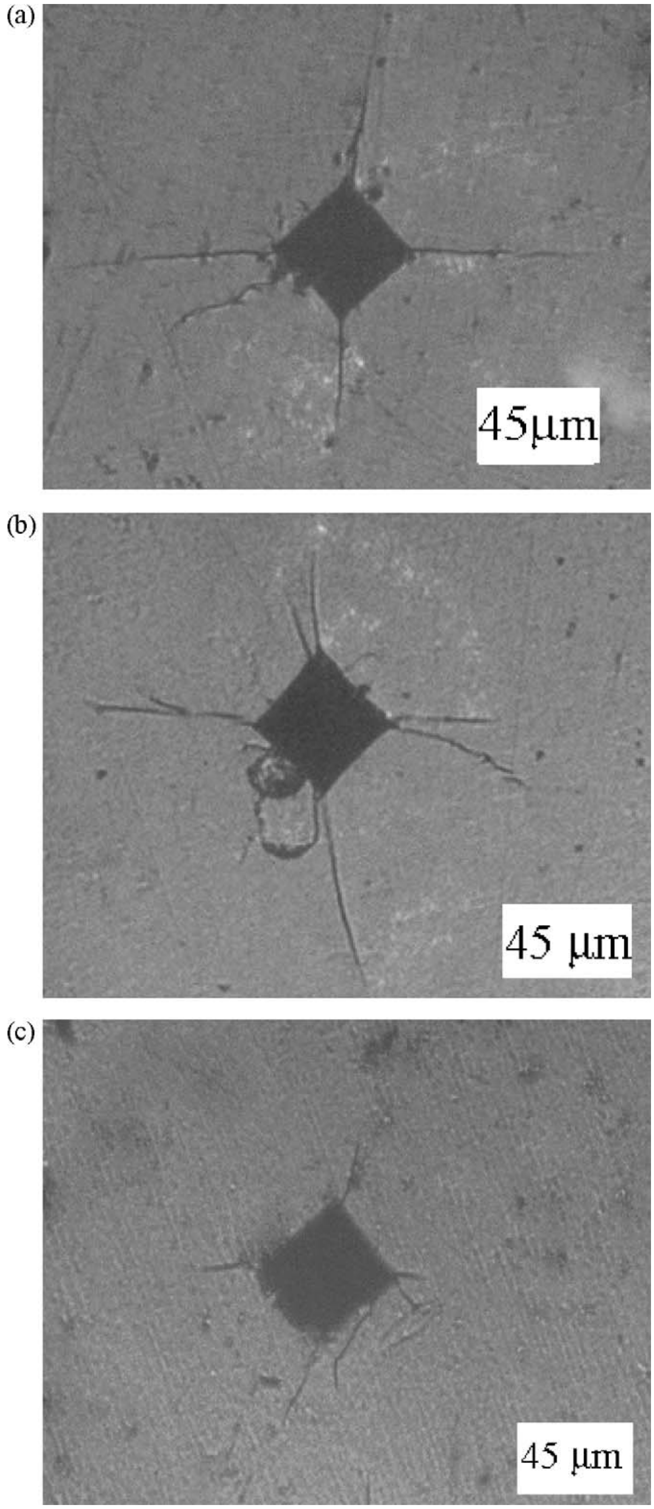

Fig. 21. (a) Image of polished surfaces of pure HAP samples after the Vickers test, MW sintered at 1200 °C. (b) Image of polished surfaces of pure HAP samples after the Vickers test, MW sintered at 1100 °C. (c) Image of polished surfaces of pure HAP samples after the Vickers test, MW sintered at 900 °C.

values of the fracture toughness of the MW sintered monophase HAP ceramics with smaller grain size.

The images of polished surfaces of the pure HAP samples, microwave sintered at 1200 °C, 1100 °C and 900 °C after the Vickers test are presented in Figs. 21a–c. These pictures demonstrate that the fracture cracks after the Vickers test of the sample with smaller grains are certainly shorter than the cracks in the samples obtained at higher temperatures, with larger grains.

Table 1
Processing conditions and mechanical properties of monophase HAP1 bioceramic materials obtained using conventional and microwave sintering.

Temperature of sintering, °C	900	900	1000	1000
Type of sintering	Conventional	Microwave	Conventional	Microwave
Holding time, min	120	15	120	15
Hardness, GPa	2.75	3.45	3.95	4.19
Fracture toughness, MPa m$^{1/2}$	0.77	1.30	0.89	1.04

The fracture toughness and hardness of pure HAP samples microwave sintered at 900 °C and 1000 °C with a holding time of 15 min and those conventionally sintered at the same temperatures with a holding time of 2 h are given in Table 1.

According to these results, it can be concluded that the fracture toughness and hardness of the monophase MW sintered HAP samples are definitely higher than those of the samples obtained by the conventional method. The difference between the mechanical properties of the conventional and microwave sintered HAP bioceramics are greater at 900 °C than at 1000 °C.

4. Conclusions

Fine grain sized pure HAP and biphasic HAP/TCP biomaterials were processed by microwave sintering, starting from stoichiometric and calcium deficient nanosized HAP powders. The processed samples without cracks or deformations with uniform shrinkage confirmed the very good sinterability of nanocrystalline HAP powders under microwave furnace conditions.

The microstructures of the monophase HAP samples microwave sintered for 15 min in the range of temperature 900–1200 °C were dense and uniform, with a mean grain size in the range from 130 nm to 1.59 μm. A calcium deficient HAP powder was transformed through microwave sintering at 900 °C and 1000 °C for 15 min into fine grained HAP/β-TCP compacts but at higher temperatures, the β-TCP transformed into α-TCP, which resulted with a small expansion and a decrease of the linear shrinkage. With the increasing of sintering temperature from 900 °C to 1200 °C, the grain size of the HAP/TCP bioceramics increased more rapidly than during the formation of pure HAP bioceramics, from 100 nm to 4.70 μm.

The monophase HAP bioceramics had appreciably higher values of the fracture toughness than the biphasic HAP/TCP bioceramics. Reducing the microwave sintering temperature and decreasing of the grain size resulted in an increase in the difference of the fracture toughness values of the HAP and HAP/TCP materials.

The decrease in the grain size of the microwave sintered HAP bioceramic from 1.59 μm to 240 nm resulted in an increase of the fracture toughness from 0.85 MPa $m^{1/2}$ to 1.04 MPa $m^{1/2}$, while the maximum value of the fracture toughness, 1.30 MPa $m^{1/2}$, was attained with the pure HAP sample with lowest mean grain size of 130 nm. The hardness of the microwave sintered HAP bioceramic materials were in the range from 3.45 GPa to 4.85 GPa.

By microwave sintering of nanosized HAP powders, with a holding time of 15 min, more dense and uniform microstructures were obtained than by conventionally sintered samples for 2 h at the same temperature. The fracture toughness and hardness of the pure HAP bioceramics obtained by microwave sintering were higher than those of the HAP ceramics obtained by conventional sintering.

The results of the current study suggest that microwave sintering may be employed to process fine grained HAP-based bioceramic materials with improved mechanical properties and with limited grain growth. The microstructures, phase compositions and mechanical properties of the microwave sintered bioceramics in this study indicated the potential application of the processed materials as hard tissue replacement materials.

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