J Mater Sci: Mater Med (2007) 18:883–893
DOI 10.1007/s10856-006-0091-0

Influence of oxide-based sintering additives on densification and mechanical behavior of tricalcium phosphate (TCP)

Himesh A. Bhatt · Samar J. Kalita

Received: 15 April 2005 / Accepted: 22 February 2006 /

Abstract In this research, we studied and analyzed the effects of four different oxide-based sintering additives on densification, mechanical behavior, biodegradation and biocompatibility of tricalcium phosphate (TCP) bioceramics. Selective sintering additives were introduced into pure TCP ceramics, in small quantities, through homogeneous mixing, using a mortar and pestle. The consequent powders of different compositions were pressed into cylindrical compacts, uniaxially and sintered at elevated temperatures, 1150°C and 1250°C, separately in a muffle furnace. X-ray powder diffraction technique was used to analyze the phase-purity of TCP after sintering. Hardness of these sintered specimens was evaluated using a Vickers hardness tester. Sintered cylindrical samples were tested under uniaxial compressive loading, as a function of composition to determine their failure strength. Biodegradation studies conducted using simulated body fluid under dynamic environment, revealed that these additives could control the rate of resorption and hardness degradation of TCP ceramics.

Introduction

It has been the goal of biomaterial scientists, for a while, to develop ideal bone graft materials for the repair of damaged or diseased parts of the skeletal system. An ideal bone graft material should support the activity of osteoblasts in the development of new bone, while simultaneously being resorbed by osteoclasts, as a part of the lifelong process of bone remodelling. A variety of ceramic materials have been tested and developed for use in the repair of bone defects in the human body. These novel ceramic materials are called *bioceramics*. Among them, calcium phosphate-based ceramics (CPCs) have received a great deal of attention as preferred materials for a number of biomedical applications, such as, in orthopedics, dentistry and the drug delivery industry [1–3]. CPCs exhibit considerably improved biological affinity and activity compared to existing synthetic materials.

Calcium phosphates exist in various forms and phases depending on temperature and partial pressure of water [2, 3]. Among these forms, particular attention has been placed to tricalcium phosphate [$Ca_3(PO_4)_2$, TCP] and hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAp] due to their outstanding biological responses to physiological environments [4]. The contemporary health care industry uses CPCs, depending on whether a resorbable or a bioactive material is desired. Because of the chemical similarity between HAp and the bone mineral, synthetic HAp exhibits strong affinity to host hard tissues. On the other hand, TCP has been proved to be resorbable in vivo with new bone growth, replacing the implanted TCP [5]. This property imparts significant advantage to TCP compared to other biomedical materials, which are not resorbed and replaced by natural bone [6].

Tricalcium phosphate is thermodynamically stable only at high temperatures [1,000–1,500°C]. β-TCP and α-TCP are the only two forms of TCP, known to exist. β-TCP transforms to α-TCP at around 1,200°C. The later phase is stabilized in the temperature range of

---

H. A. Bhatt · S. J. Kalita (✉)
Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL 32816-2450, USA
e-mail: samar@mail.ucf.edu

700–1,200°C [2]. α-TCP, however, has received very little interest from the biomedical field. The disadvantage for using α-TCP is its quick resorption rate, which limits its usage in this area [6]. However, β-TCP, also known as β-whitlockite, is essentially a slow degrading bioresorbable calcium phosphate ceramic [7] and is a promising material for biomedical applications such as orthopedics. It has been known to have significant biological affinity and activity, and responds very well to the physiological environments [8]. Because of its slow degradatory characteristic, the porous β-TCP is regarded as an ideal material for bone substitutes that should degrade as bone cells grow inside the scaffold [9, 10]. These factors give β-TCP an edge over other biomedical materials when it comes to resorbability and replacement of the implanted TCP in vivo by the new bone tissue [11]. β-TCP has a pure hexagonal crystal structure. It belongs to space group R3cH and its unit cell dimensions are: $a = b = 10.439$ Å, $c = 37.375$ Å, and $\alpha = \beta = 90°$, $\gamma = 120°$. It is reported that the resorbability of β-TCP in vivo might be strongly related to its structure [12]. However, although β-TCP degrades slowly compared to α-TCP form, the rate of degradation is uncontrolled [7, 8], which limits its usage in most bone engineering applications.

Another major shortcoming of β-TCP, as well as other phases of CPCs is their poor mechanical strength, in complex stress states. Like other ceramic materials, the compressive and flexural strengths of CPCs are governed by the presence of voids, pores and/or interstices, which occurs during the process of sintering and densification. However, unlike most advanced ceramics, CPCs are difficult to sinter and therefore, are mechanically weak. In this work, we endeavored to improve sinterability of β-TCP; to enhance its mechanical strength, and to control its rate of biodegradation by introducing small quantities of various oxide-based sintering additives. We investigated the effects of these additives on TCP ceramic with regard to its densification, hardness, compression strength, and in vitro degradation behavior. This paper describes the processing and characterization of metal ion doped calcium phosphate based ceramic structures with tailored rate of resorption, for possible bone-tissue engineering applications.

Experimental procedure

Materials and methods

β-TCP powders (NC/FCC grade) with the average particle size of 3 μm were acquired from Rhodia Chemicals, Chicago, IL. The TCP powder, approved by National Formulary (NF), was mixed with various sintering additives at different wt.% ratios. Sintering additives were selected based on preceding research [13–18], and the presence of metal ions in the composition of bone mineral [19]. The selected additives were magnesium oxide (MgO, Alfa Aesar, Ward Hill, MA, 96% pure), zinc oxide (ZnO, Alfa Aesar, Ward Hill, MA, 99% pure), silicon (IV) oxide (SiO_2, Alfa Aesar, Ward Hill, MA, 99.5% pure), titanium (IV) oxide, (TiO_2 anatase, Alfa Aesar, Ward Hill, MA, 99.9% pure). These additives were introduced in the TCP ceramic powder separately at different wt.% (1.0 wt.%, 2.5 wt.% and 4 wt.%), followed by homogeneous mixing in a mortar and a pestle for 30 min. Consequent powders of variant compositions were uniaxially compacted in a steel mold, with an internal diameter of 10 mm at a pressure of 37.5 MPa using a 12-ton press from Carver Inc., Wabash, IN (3851–0 Model C). Compositions of powder mixture of TCP with different sintering additives are presented in Table 1.

Green ceramic structures were measured for their density and then sintered in a muffle furnace, in air, at different sintering temperatures, 1,150°C and 1,250°C, separately for 6 h. A sintering cycle was developed to achieve better densification and to avoid cracks in the sintered specimens by introducing several soaking temperatures and tailoring the rate of heating and cooling. The consequent cycle had several steps: first, infusion at 150°C to stabilize the furnace; second, infusion at 550°C to remove residual stresses from the green structures; and the final infusion at 1,150°C or 1,250°C for densification. A slow heating rate of 1°C/min was used for better densification. Sintered ceramic structures were measured for their density and then,

Table 1 Compositions of calcium phosphate ceramics studied

Type	Base powder: pure TCP	
	Additive composition (wt.%)	
TCP	—	—
A1.0	1.0%	MgO
A2.5	2.5%	MgO
A4.0	4.0%	MgO
B1.0	1.0%	ZnO
B2.5	2.5%	ZnO
B4.0	4.0%	ZnO
C1.0	1.0%	SiO_2
C2.5	2.5%	SiO_2
C4.0	4.0%	SiO_2
D1.0	1.0%	TiO_2
D2.5	2.5%	TiO_2
D4.0	4.0%	TiO_2

were subjected to mechanical characterization and bioresorbability analysis. Samples sintered at 1,150°C showed poor densification and, therefore, were not characterized for their mechanical and biodegradation behavior.

Phase identification and microstructural analysis

X-ray powder diffraction (XRD) technique was used to study the effect of sintering temperature and additives on phase purity of TCP ceramics. Sintered ceramic structures of variant composition were crushed and ground to fine powder, manually, using a mortar and a pestle. Powder samples of variant composition (TCP, A1.0, B1.0, C1.0 and D1.0) were placed in the specimen holder of Rigaku diffractometer, separately, and then analyzed, using Ni-filtered CuK_α radiation ($\lambda = 0.1542$ nm) at 40 kV and 40 mA settings. The XRD patterns were recorded in the 2θ range of 15°–65°, with a step size of 0.02° and step duration of 0.5 s.

Scanning electron microscopy (SEM) was used to observe and analyze the microstructure of sintered ceramic structures to study and understand the influence of sintering aids on grain size and surface porosity after sintering. Specimens of pure TCP and TCP reinforced with 1.0 wt.% of additives (A1.0, B1.0, C1.0, and D1.0) sintered at 1,250°C for 6 h, were only observed under SEM for microstructural analysis. Specimens used for SEM examination had average dimensions of 8 mm in diameter and 2.3 mm in thickness. These specimens were gold-coated for 1 min using a magnetron sputter coater from Emitech Inc. and placed inside a Jeol SEM, Model 6400F (Tokyo, Japan) for observation.

Mechanical characterization

Mechanical properties of sintered ceramic structures containing various sintering additives were evaluated in terms of their hardness and compression strength. Sintered ceramics of all composition types (TCP, A1.0, B1.0, C1.0, D 1.0, A2.5, B2.5, C2.5, and D2.5) were indented with a Vickers diamond indenter and the indentation size was measured automatically to find their hardness in a Vickers hardness tester (LECO 700). Specimens used for hardness testing had an average dimension of 8 mm in diameter and 2.3 mm in thickness. The test was carried out with a major load of 1 kg for 5 s loading. Two samples of each of the composition type were tested for their hardness at three different locations. The average of these readings were calculated and compared for analysis.

To determine mechanical strength under uniaxial compressive loading, the sintered ceramic specimens of selected compositions (TCP, A1.0, B1.0, C1.0, and D1.0) were tested in a fully automated tensile tester from Instron (Model 3369) with a constant crosshead speed of 1 mm/min. Six cylindrical samples of each of these compositions with diameter to height ratio of 1:1.5 (approx.) were prepared and then sintered at 1,250°C for 6 h. The compression samples had an average diameter of 7.5 mm with an average height of 11.5 mm. Only samples containing 1.0 wt.% of additives were subjected to compression testing.

Biodegradation study

The rate of degradation of sintered ceramic structures of different compositions was determined in terms of their weight-loss in a protein free dynamic simulated body fluid (SBF). SBF has been widely used by researchers to test bioactivity of materials by examining the formation of apatite layer on the surface of testing materials. The in vivo formation of an apatite layer on the surface of a bone grafting material can be reproduced in acellular SBF which is prepared to have an ion concentration nearly equal to that of human blood plasma [20–22] (Na^+ 142.0, K^+ 5.0, Ca^{2+} 2.5, Mg^{2+} 1.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, and SO_4^{2-} 0.5 mM, and a pH of 7.3, as shown in Table 2. In our work, we used SBF to determine effect of selected sintering additives on biodegradation of TCP. Samples containing 1.0 wt.% of additives were prepared and immersed in a dynamic SBF solution for weeks. A tank having compartments for placing the samples separately was selected. A set of fifteen samples of composition types TCP, A1.0, B1.0, C1.0 and D1.0 were placed in perforated plastic containers and then

Table 2 Ionic concentration of human blood plasma and SBF

	Ionic concentration (mM)							
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
Human blood plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5
SBF	142.0	5.0	1.5	2.5	148.8	4.2	1.0	0.5

SBF buffered at pH 7.3 with tris-hydroxymethylaminomethane and 1 M HCl these containers were placed inside the tank. The tank was filled with freshly prepared SBF and was observed for 5 weeks, in a state of constant flow. SBF was replaced every week with a freshly prepared one to maintain its ionic concentration. At the end of each week, three samples of each of these compositions were taken out from the tank, dried at 100°C in a furnace and measured for their weight to calculate weight loss as a result of time. Dried specimens were also tested for their hardness, to understand the effect of biodegradation on their mechanical property.

Results

Densification study

Green ceramic structures prepared via uniaxial pressing were measured for their bulk density and were subjected to pressure-less sintering. Two sets of four green specimens of all composition types (TCP, A1.0, B1.0, C1.0, D 1.0, A2.5, B2.5, C2.5, D2.5, A4.0, B4.0, C4.0 and D4.0) were sintered at 1,150°C and 1,250°C separately, for 6 h to study the effect of sintering temperature and the amount of sintering additives on densification of TCP. Each sintered specimen was measured for its bulk density and the average of each of the compositions. The average sintered densities for different compositions were plotted as a function of percentage of sintering additives at two different temperatures, 1,150°C and 1,250°C and are presented in Fig. 1a and b. It is evident from Fig. 1a that sintering at 1,150°C did not improve densification of TCP. The highest sintered density of 2.77 g/cc was recorded for composition type B1.0 at 1,150°C. Pure TCP showed a maximum density of 2.50 g/cc at this temperature. Results of sintering at 1,250°C showed that the maximum sintered density of 3.39 g/cc could be achieved in structures of composition A1.0 (1.0 wt.% addition of MgO). Pure TCP, sintered at this temperature, showed a density of 3.04 g/cc.

Figure 1c presents the plot of volume shrinkage as a function of composition for specimens sintered at 1,250°C. Maximum volume shrinkage was observed for the composition A1.0 while composition D2.5 showed the minimum value of volume shrinkage. Composition B2.5 showed nearly the same volume shrinkage as that of pure TCP, which was 53%.

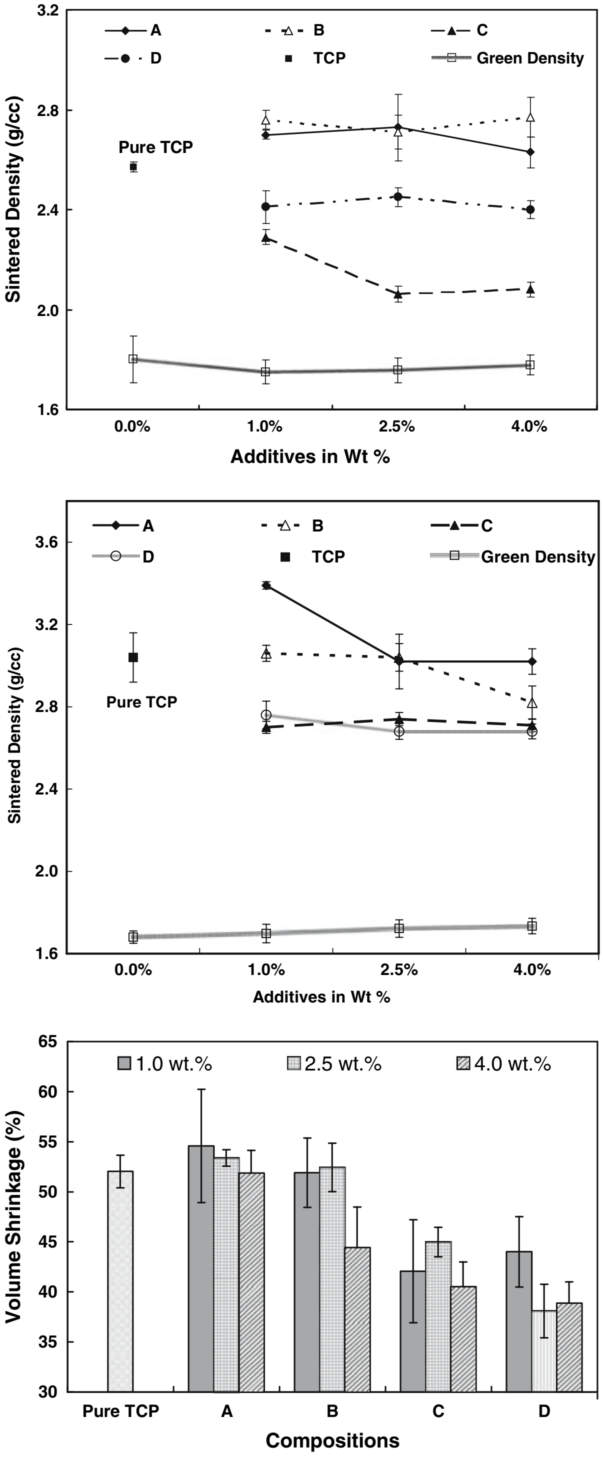


Fig. 1 (**a**) Influence of oxide-based sintering additives on densification of tricalcium phosphate (TCP) ceramics. Sintering was done at 1,150°C for 6 h. (**b**) Influence of oxide-based sintering additives on densification of TCP. Sintering was done at 1,250°C for 6 h. (**c**) Effect of additives on volume shrinkage of TCP ceramics sintered at 1,250°C

Phase identification and microstructural analysis

Results of X-ray powder diffraction revealed that presence of sintering additives and sintering temperature (1,250°C) did not alter the phase purity of TCP ceramics. Figure 2 shows X-ray diffraction patterns of sintered for the compositions TCP, A1.0, B1.0, C1.0 and D1.0. Peaks in each X-ray diffraction pattern were recorded and verified using standard JCPDS file, no. 9–169. Compared to XRD pattern of pure TCP, the crystallinity of TCP increased on addition of some of the sintering additives but no obvious phase change was noticed from these XRD patterns. Almost identical patterns were recorded for all these compositions, which suggest that the presence of 1.0 wt.% of sintering aids did not alter phase-purity of TCP. Compositions with higher percentage of sintering additives were not analyzed for their phases.

Sintered ceramic structures were observed under an SEM to understand, compare and analyze the effects of sintering additives on microstructure and correlate them with physical and mechanical properties. Results of SEM are shown in Fig. 3a–d, and e for structures sintered at 1,250°C of composition type TCP, A1.0, B1.0, C1.0 and D1.0, respectively. Micrographs of all of these compositions showed clear demarcation in the grain boundaries and therefore, their grain diameter could be easily calculated. Linear intercept method was employed to calculate average grain diameter of the sintered structures. The average grain sizes were calculated to be 3.14 μm, 4.19 μm, 3.19 μm, 7.23 μm and 6.81 μm, respectively, for composition types TCP, A1.0, B1.0, C1.0 and D1.0.

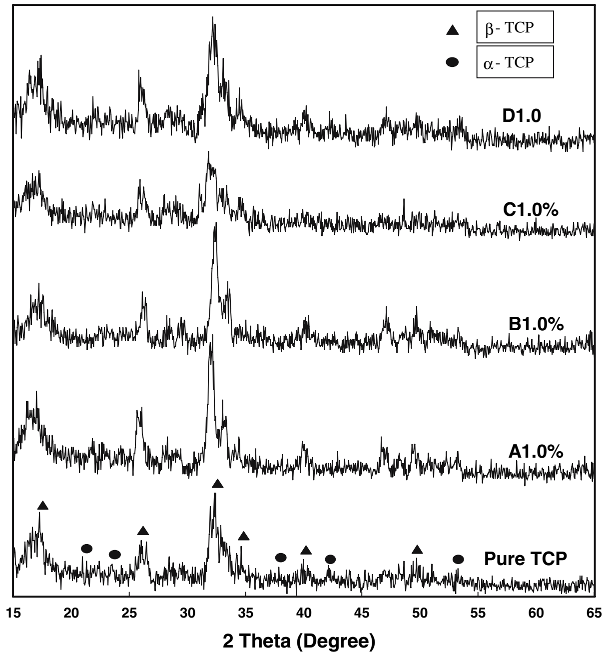


Fig. 2 XRD patterns of sintered TCP ceramics doped with 1.0 wt.% of various oxide-based sintering additives. Sintering was done at 1,250°C

Mechanical property evaluation

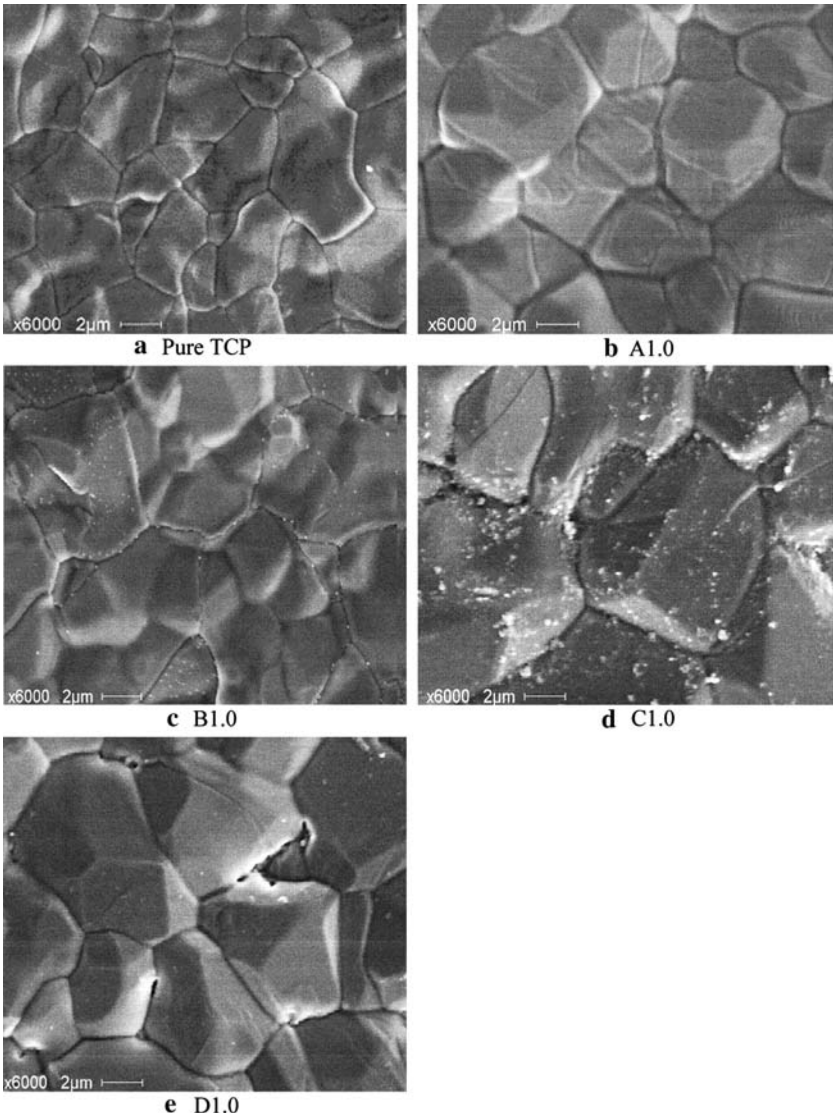
Vickers hardness testing

Results of Vickers hardness testing revealed that the presence of some of these sintering additives could significantly enhance the hardness of TCP ceramics. Hardness testing was performed on specimens of pure TCP and TCP containing 1.0 wt.% and 2.5 wt.% of additives (TCP, A1.0, B1.0, C1.0, D 1.0, A2.5, B2.5, C2.5, and D2.5), sintered at 1,150°C and 1,250°C, separately. The average hardness of each of these composition types was calculated and plotted as a bar chart as shown in Fig. 4 as a function of composition. It can be observed from Fig. 4, presence of sintering additives influenced hardness of TCP both positively and negatively. With respect to sintered structure of pure TCP, some composition types showed higher hardness while some other compositions showed relatively lower hardness. In accordance with our densification studies, specimens sintered at 1,150°C showed significantly lower hardness in comparison to the specimens sintered at 1,250°C. The highest hardness value of 302 HV was achieved for the composition type A1.0 sintered at 1,250°C, which had also shown the highest sintered density. At 1,250°C, composition types A1.0, A2.5, B1.0, B2.5, and D1.0 showed enhanced hardness compared to pure TCP although some of these compositions showed nearly equal or lower sintered density than pure TCP. We believe that the presence of additives improved grain boundary properties of TCP thereby improving its mechanical property. Composition type C1.0 showed a hardness value very close to that of pure TCP in spite of its low sintered density (Fig. 1b) and higher grain size (Fig. 2d). To bring out the relationship between sintered density and hardness, separate graphs showing variation of hardness as a function of sintered density for structures sintered at 1,150°C and 1,250°C. These graphs are shown in Fig. 5a and b.

Compression testing

TCP ceramics integrated with 1.0 wt.% of different sintering additives were subjected to mechanical testing to determine their failure strength under uniaxial compressive loading. Sintered ceramic structures with average dimensions of 7.5 mm in diameter and 11.5 mm in height of composition types TCP, A1.0, B1.0, C1.0, and D1.0 were evaluated for their compression strength in a fully automatic screw driven tensile tester from Instron. These tests were carried

Fig. 3 SEM micrographs of sintered TCP containing various additives



a Pure TCP **b** A1.0 **c** B1.0 **d** C1.0 **e** D1.0

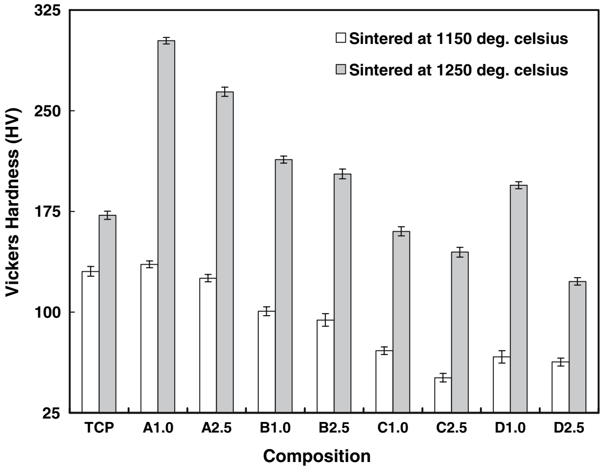


Fig. 4 Effect of additives on hardness of TCP ceramics sintered at different temperatures

out with a constant crosshead speed of 1.0 mm/min. Average compression strengths of different compositions were evaluated and were compared with that of pure TCP structures processed under the same conditions. Results of compression testing are shown in Table 3. The maximum compression strength of 91 MPa was achieved for composition A1.0. Pure

Table 3 Compressive strengths of pure TCP and TCP reinforced with 1.0 wt.% of additives

Type	Compression strength (MPa)
TCP	29.7 (±4.2)
A1.0	90.9 (±5.1)
B1.0	71.3 (±3.1)
C1.0	41.5 (±4.2)
D1.0	29.9 (±2.2)

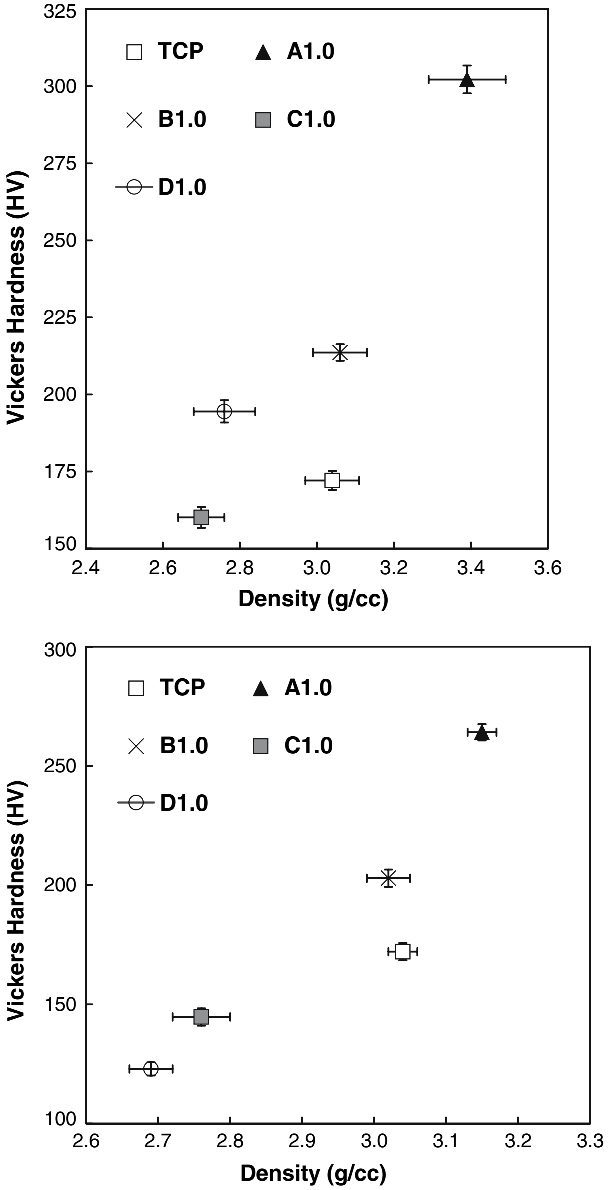


Fig. 5 (**a**) Density versus hardness plots for dense TCP structures containing 1.0 wt.% of additives sintered at 1250°C. (**b**) Density versus hardness plots for dense TCP structures containing 2.5 wt.% of sintering additives sintered at 1,250°C

TCP, processed under the same conditions, showed an average compressive strength of 30 MPa. Although structures of composition type C1.0 and D1.0 showed poor densification and relatively lower hardness, their compressive strengths (42 MPa and 30 MPa) were close to or slightly higher than that of pure TCP.

Biodegradation study

Biodegradation study conducted in SBF, maintained in a dynamic state, showed that these sintering additives could tailor the rate of resorption of TCP ceramics.

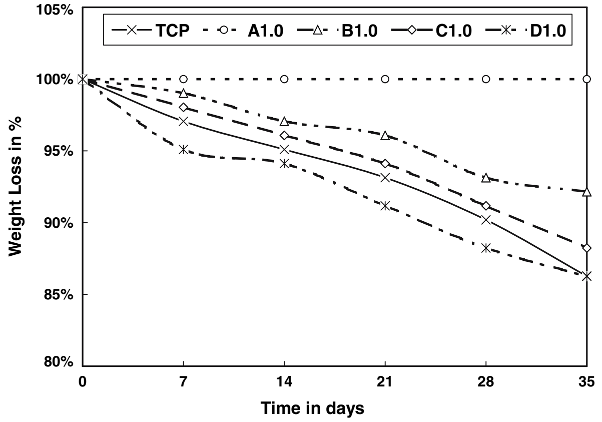


Fig. 6 Biodegradation of metal ion-doped sintered TCP in a dynamic simulated body fluid (SBF)

Figure 6 shows the rate of resorption of sintered ceramics structures of different composition measured in terms of their weight loss at different time points. It is clear from Fig. 6 that composition type A1.0 showed no obvious weight loss during the five week degradation study where as for all other compositions (TCP, B1.0, C1.0 and D1.0), there was an increase in weight loss with time.

Influence of sintering additives on the degradation of mechanical behavior of TCP ceramics was studied by evaluating the hardness of sintered specimens of different compositions, as they dissolved in SBF, with time. A set of two specimens of each composition type was removed from the SBF solution at set time points (day 7, 14, 21, 28 and 35) and tested in a Vickers hardness tester in three different locations. The average hardness was calculated for each composition at separate time points. The results were plotted as a function of time, as shown in Fig. 7; where hardness is expressed in percentage with respect to the hardness of pure TCP structure prior to immersion in SBF. It is apparent from Fig. 7 that for composition type A1.0, no decrease in hardness was observed for the five-week dissolution study. However, for all other composition types (TCP, B1.0, C1.0 and D1.0), hardness decreased with time, in different rates. Composition types C1.0 and D1.0 showed a continuous decline in hardness, whereas; for B1.0 the rate of decrease in hardness was marginal. Structures of A1.0 and B1.0 maintained much higher hardness compared to pure TCP structure, throughout the experiment.

Discussion

Use of sintering additive is a well-documented approach to improve mechanical performance of ceramic materials. This established method has also

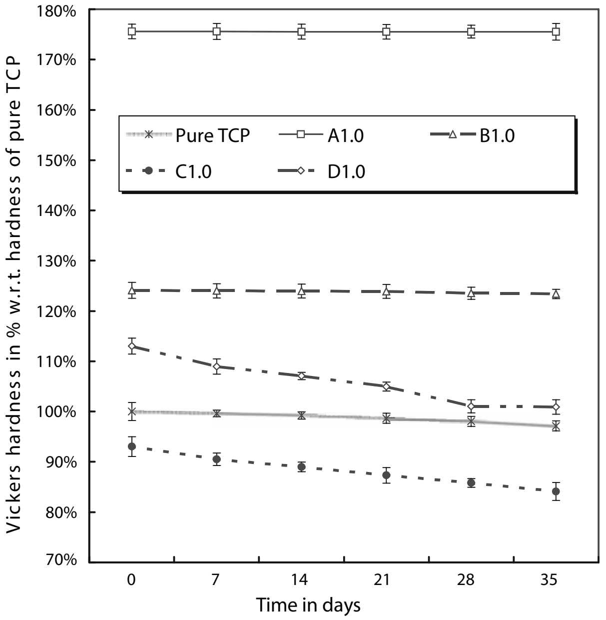


Fig. 7 Effect of biodegradation on hardness of TCP ceramics doped with different sintering additives at various time points

been explored to improve mechanical properties of calcium phosphate bioceramics, *viz.*, HAp, by improving densification during sintering [13–15, 23]. Researchers also improved the mechanical properties of HAp through liquid-phase sintering, using glasses as the secondary phase [16, 18, 24]. Nevertheless, whether it is solid-state or liquid-phase sintering, a careful selection of additives is of high importance in biomaterial research, to avoid potential contamination. Contamination can be detrimental to bioceramics, where biocompatibility is a crucial issue depending strongly on composition. Quantity of the additives and the development of a material-specific sintering cycle are other key factors in achieving the desired properties. β-TCP bioceramic is known for its excellent biocompatibility and osteoconductivity [8]. Therefore, utmost care was taken in selecting additives for β-TCP. MgO, ZnO, SiO_2 and TiO_2 were selected, based on literature [13–18, 23] and our previous research [15, 17]. Another criterion for this choice is the natural presence of some of these metal ions in bone mineral.

Results of our research revealed that MgO, ZnO, SiO_2 and TiO_2 could be used as additives to improve/tailor densification, hardness, strength and biodegradation characteristics of β-TCP ceramics. X-ray powder diffraction analysis of the sintered TCP doped with these additives confirmed that their presence does not alter the phase purity of TCP. Further, sintering temperature and time did not lead to phase transformation appreciably. JCPDS file, no 9–169 used to identify the peaks of beta calcium orthophosphate (β-TCP, β-$Ca_3(PO_4)_2$) showed the presence of all major peaks. XRD analysis also revealed that some of these additives improved crystallinity of β-TCP. Peaks of relatively higher intensity were recorded for compositions A1.0 and B1.0 compared to pure β-phase.

Results of the sintering study show that these additives affect the densification of β-TCP, both positively and negatively (Fig. 1a, b). Sintering at 1,250°C significantly improved the densification of all compositions including pure TCP, in comparison to sintering at 1,150°C. Results of sintering at 1,250°C for 6 h showed a remarkable improvement (11.5%) in sintered density in composition A1.0, compared to pure TCP. Sintering at 1,250°C also improved the sintered density in compositions B1.0 and B2.5 marginally, compared to pure TCP. It was observed that the addition of SiO_2 (C1.0, C2.5, C4.0) and TiO_2 (D1.0, D2.5, D4.0) negatively influenced the densification of TCP (Fig. 1a, b). From these results we can conclude that pressure-less sintering at 1,250°C is more favorable for better densification than 1,150°C. However, no general relation between the amount of additive and sintered density could be deduced from our results. This relationship varied from one composition to another, which is in line with works reported by other researchers [13, 16, 24]. For compositions A, B and D, 1.0 wt.% addition showed the highest density, whereas for composition C, 2.5 wt.% addition showed the highest density when sintered at 1,250°C. Our results of sintered density correlate well with the volume shrinkage recorded on these samples (Fig. 1c). The maximum volume shrinkage and the highest sintered density were observed for composition A1.0. With an increase of the additive amount (composition A) the shrinkage reduced along with their density. For composition B, the maximum shrinkage was observed in 2.5 wt.% addition (B2.5); though, the highest density was recorded in 1.0 wt.% addition (B1.0). This anomaly can be ignored considering the marginal difference between sintered densities of these two compositions, i.e., 3.06 ± 0.07 in B1.0 and 3.04 ± 0.03 g/cc in B2.5. In compositions C and D, the volume shrinkage related well with sintered density, i.e., higher the shrinkage the greater is the sintered density.

Results of Vickers hardness testing proved that the surface hardness of β-TCP could be improved/tailored by introducing these sintering additives in small quantities. As seen in Fig. 4, the only additive which showed higher hardness compared to pure TCP was 1.0 wt.% of MgO (Composition A1.0), when the specimens were sintered at 1,150°C. Whereas, hardness testing on specimens sintered at 1,250°C clearly showed an increase in hardness compared to pure TCP (Compositions A1.0, A2.5, B1.0, B2.5 and D1.0). The maximum overall hardness of 302 ± 2.5 HV was recorded in composition A1.0. Pure β-TCP exhibited hardness of 172.1 ± 3.1 HV, which represents 76% improvement for composition A1.0, 53% increase for composition A2.5, 24% increase for composition B1.0, 18% increase for composition B2.5 and 13% increase for composition D1.0. The results of hardness testing conjugate well with our densification results. Figure 5a and b bring out the relationship between sintered density and hardness. It is evident from the figures that hardness improved the sintered density increase. It is worth noting that some of the additives (A2.5, B2.5 and D1.0) improved hardness of TCP though their presence did not improve the sintered density. One of the possible rationales as to why these additives improved mechanical properties has to deal with the grain boundaries. Our hypothesis is that the presence of additives possibly improved the grain boundary properties of β-TCP. An in-depth understanding on how each additive influences TCP may be made possible through extensive TEM investigation of the grain boundaries; which could not be accomplished here.

Another major improvement was achieved in the compression strength of TCP ceramics when doped with 1.0 wt.% of these additives. Composition type A1.0 showed the highest failure strength (90.9 MPa) under compressive loading, which is a 206% improvement, compared to compression strength of pure TCP structures (29.9 MPa), processed under the same conditions. Composition types B1.0 and C1.0 showed 140% and 40% increase in compression strength over pure TCP. It is important to note that mechanical properties of uniaxially compacted sintered structured depend on many variables including compaction, green density of pellets, surface finish of the mold used in compaction, sintering time, temperature, as well as, environment. Structures prepared *via* high pressure pressing routes such as cold isostatic pressing and hot isostatic pressing will possibly possess even higher mechanical properties. Variations in the additives' influence on β-TCP can be attributed to their quantity, phase transformation of β-TCP, and possible substitution of these ions in the β-TCP lattice. Enderle et al. studied the influence of magnesium doping on β-TCP and found that the transformation temperature of β-TCP to α-phase increased from 1,150°C without Mg^{2+} to 1,540°C with Mg^{2+} substitution on Ca^{2+} sites [25]. Some of the variations in physical and mechanical properties of TCP ceramics doped with different quantities of MgO, ZnO, SiO_2 and TiO_2 as additives, as seen in this research, can be better explained using the results from our SEM examination.

SEM results showed that the presence of sintering additives increased the grain-size of the sintered ceramics compared to pure TCP, processed under the same conditions. The grain growth was significant for composition types C1.0 and D1.0, which explains the low sintered density compared to pure TCP. From their micrographs, it is also visible that these structures had surface porosity, which hindered proper densification during sintering. Compositions TCP and B1.0, sintered at 1,250°C, showed very little difference in both their grain sizes and sintered densities. In contrast, composition A1.0 showed significantly improved sintered density although its grain size (4.19 µm) was slightly higher than that of pure TCP (3.14 µm). Our explanation for this is that although there was a marginal increase in grain size for composition A1.0, the sintering additive possibly improved the grain boundary properties; thereby, improving its sintered density and other mechanical properties. SEM micrograph of this composition (Fig. 3b) shows that the sintered structure was fully dense without any surface porosity, voids or cracks, which improved its properties. Also from Fig. 3d and e, it is apparent that the structure had surface cracks and voids along the grain boundaries, which contributed to poor densification and other mechanical properties compared to composition A1.0 and B1.0. For composition B1.0, the mechanical properties were inferior to that of composition A1.0 in spite of smaller grain size (3.19 µm), possibly because of its lower sintered density and associated lower volume shrinkage. From the SEM micrograph of composition B1.0 (Fig. 3c), it can also be seen that though the grains are smaller and visible, their grain boundaries are not distinct. Possibly under the given sintering conditions, some of these grains are on the verse of coalescence, which has possibly led to lower mechanical properties and poor densification than composition A1.0. Tailoring of sintering variables and atmosphere might further improve the properties of compositions B, C and D. SEM micrographs also provide the explanation as to why compositions A1.0, B1.0 and C1.0 showed significantly higher compression strength compared to pure TCP. As seen in Fig. 3a, composition A1.0 had almost equiaxed grains with no pores, and had the highest compression strength. Although pores were present in both C1.0 and D1.0 (Fig. 3d, e), the pores were larger in D1.0 compared to C1.0. This explains why C1.0 showed higher compression strength than D1.0.

Based on our research results, we conclude that MgO, ZnO, SiO_2 and TiO2 ceramics can be used as sintering additives to enhance/tailor mechanical properties of β-TCP without undergoing significant phase changes. Our results are in line with the work of Georgiou et al. [13], Santos et al. [24], Kalita et al. [15], Knowles et al. [16] and Suchanek et al. [23] where they have studied the influence of sintering additives and glass additions on densification and mechanical properties of HAp ceramics. Yet, to our knowledge, no such work has been reported on TCP. Recently, some attention has been given on β-TCP research. Reid et al. discussed the effects of silicon substitution on phase evolution in TCP/apatite system [26]. Ito et al. evaluated the resorbability and solubility of zinc-containing TCP and found that the solubility decreased with increasing zinc content [27]. They also reported that zinc has stimulatory effects on bone formation, in vitro and in vivo [28].

In vitro studies were performed to study biodegradation behavior and surface hardness deterioration of TCP doped with various sintering additives in SBF. Results (Fig. 6) revealed that these additives could tailor the rate of resorption of TCP. Practically no degradation (weight loss) was observed in composition A1.0 even after 35 days of immersion in SBF, maintained in dynamic state. This composition also showed no deterioration of surface hardness during the five-week study (Fig 6). For pure β-TCP, an appreciable amount of hardness degradation was observed, which also showed significant weight loss. Relatively slow rate of degradation was observed in composition B1.0, which also exhibited very slow surface hardness deterioration. However, for composition C1.0 and D1.0, the decrease in hardness and weight loss were significant. It is worth noting that though there was an appreciable weight loss for composition B1.0, the deterioration of hardness was negligible, which indicate that the structures were able to maintain mechanical properties even though they were being degraded over time. Maintenance of mechanical properties during the degradation period is essential towards the development of viable resorbable bone-grafts with controlled strength-loss. Though our biodegradation study in SBF showed promising results, further in vitro and in vivo experimentation are critically essential and a must for successful use of these bioceramics as bone-grafts. Due to lack of facility and resources, these studies could not be performed along with this work.

Summary and conclusions

Influence of oxide-based sintering additives on the densification, microstructure, hardness, mechanical strength and biodegradability of TCP ceramics was studied. Uniaxially compacted ceramic structures were sintered at 1,150°C and 1,250°C separately, in a muffle furnace, and were characterized for different properties. Phase analysis using X-ray powder diffraction technique revealed that the presence of these additives did not alter the phase purity of TCP ceramics. Densification results proved that sintered density of TCP ceramics could be significantly improved by the incorporation of these sintering additives (MgO, ZnO, SiO_2, and TiO_2) in small quantities. A maximum sintered density of 3.39 g/cc was achieved for the composition type A having 1.0 wt.% sintering additives, sintered at 1,250°C for 6 h. Although some of the composition types did not show improved densification, they showed improvement in hardness, in comparison to TCP ceramics. A total of 13%–76% increase in hardness was recorded for some of the compositions when tallied to pure TCP structures processed under similar conditions. Results of mechanical testing under uniaxial compressive loading showed a three-fold increase in compression strength for composition type A1.0 compared to pure TCP. Maximum compression strength of 90.9 (±5.1) MPa was achieved in this composition. Biodegradation studies conducted in dynamic SBF brought out the fact that these additives could tailor the rate of degradation of TCP, as per requirements. Understanding in vitro biological properties of these novel ceramics is the next challenge in research we will undertake, which will be accomplished as a separate project, in the future.

Acknowledgements The authors acknowledge the University of Central Florida for financial support in this research. The authors also acknowledge the experimental support by Soon Jik Hong and editorial help by Chayanika D. Kalita. Assistance from Materials Characterization Facility of the University of Central Florida is thankfully recognized, as well.

References

1. L. HENCH and J. WILSON, *Introduction to Bioceramics* (World Scientific, Singapore, 1993) p. 181
2. K. DE GROOT, C. P. A. T. KLEIN, J. G. C. WOLKE and J. M. A. BLIECK-HOGERVORST, “Handbook of Bioactive Ceramics”, In *Calcium Phosphate and Hydroxylapatite Ceramics*, Vol. 2, edited by T. Yamamuro, L. L. Hench and J. Wilson, CRC Press, Boca Raton, FL (1990), p. 3
3. L. L. HENCH, *J. Am. Ceram. Soc.* **81** (1998) 1705
4. H. MONMA, A. MAKISHIMA, M. MITZMO and T. IKEGAMI, *J. Ceram. Soc. Jpn* **96** (1988) 878
5. B. D. RATNER, A. S. HOMAN, F. J. SCHOEN and E. LEMON, *Biomaterials Science* (California: Academic Press, 1996), p. 1
6. D. S METSGER, M. R. RIEGER, D.W. FOREMAN, *J Mater Sci. Mater Med.* **10** (1999) 17

7. F. C. M. DRIESSENS, J. W. E. DIJK VAN and J. M. P. M. BORG-GREVEN, *Calcif Tissue Res.* **26** (1978) 127
8. N. KIVRAK, A. C. TAS, *J. Am. Ceram. Soc.* **81** (1998) 2245
9. M. JARCHO, R. L SALSBURY, M. B. THOMAS and R. H. DOREMUS, *J. Mater. Sci.* **14** (1979) 142
10. K. DE GROOT, *J. Ceram. Soc. Jpn*. **99** (1991) 943
11. I. R. GIBSON, I. REHMAN, S. M. BEST and W. BONFIELD, *J. Mater Sci. Mater Med* **12** (2000) 799
12. M. OKAZAKI and M. SATO, *Biomaterials* **11** (1990) 573
13. G. GEORGIOU and J. C. KNOWLES, *Biomaterials* **20** (2001) 2811
14. S. J. KALITA, S. BOSE, H. L. HOSICK and A. BANDYOPADHYAY, *Biomaterials* **25** (2004) 2331
15. S. J. KALITA, D. ROKUSEK, S. BOSE, H. L. HOSICK and A. BANDYOPADHYAY, *J. Biomed. Mater. Res. Part A* **71A** (2004) 35
16. J. C. KNOWLES, S. TALAL and J. D. SANTOS, *Biomaterials* **17**(14) (1996) 1437
17. S. J. KALITA, S. BOSE, H. L. HOSICK and A. BANDYOPADHYAY, ‘‘Bioceramics: materials and applications IV, ceramic transactions’’, vol. 147, *Proceedings of 105th Annual meeting of the American Ceramic Society, April*, edited by Veeraraghavan (V) Sundar, Richard P. Rusin and Claire A. Rutiser (2003)
18. M. A LOPES, J. D. SANTOS, F. J. MONTEIRO and J. C. KNOWLES, *J. Biomed. Mater. Res.* **39** (1998) 244
19. R. Z LEGEROS and J. P LEGEROS, *Dense Hydroxyapatite. In An Introduction to Bioceramics*, edited by L. L. Hench and J. Wilson (World Scientific Publishing Co., Singapore, 1993) p. 139
20. T. KOKUBO, S. ITO, Z. T. HUANG, T. HAYASHI, S. SAKKA, T. KITSUGI and T. YAMAMURO, *J. Biomed. Mater. Res.* **24** (1990) 331
21. T. KOKUBO, *J. Non-Cryst Solids* **120** (1990) 138
22. C. OHTSUKI, H. KUSHITANI, T. KOKUBO, S. KOTANI and T. YAMAMURO, *J. Biomed. Mater. Res.* **25** (1991) 1363
23. W. SUCHANEK, M. YASHIMA and M. YOSHIMURA, *Biomaterials* **18** (1997) 923
24. J. D. SANTOS, P. L. SILVA, J. C. KNOWLES, S. TALAL and F. J. MONTEIRO, *J. Mat. Sci. Mater. Med*. **7** (1996) 187
25. R. ENDERLE, F GOTZ-NEUNHOEFFER, M GOBBELS, F.A. MULLER and P. GREIL, *Biomaterials* **26** (2005) 3379
26. J. W. REID, A. PIETAK, M. SAYER, D. DUNFIELD and T. J. N. SMITH, *Biomaterials* **26** (2005) 2887
27. A. ITO, H. KAWAMURA, S. MIYAKAWA, P. LAYROLLE, N. KANZAKI, G. TREBOUX, K. ONUMA and S. TSUTSUMI, *J. Biomed. Mater. Res.* **60** (2002) 224
28. A. ITO, M. OTSUKA, H. KAWAMURA, M. IKEUCHI, H. OHGUSHI, Y. SOGO and N. ICHINOSE, *Curr. Appl. Phys.* **5** (2005) 402