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Short communication

Novel machinable calcium phosphate/$CaTiO_3$ composites

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Abstract

Hydroxylapatite/$CaTiO_3$ and tricalcium phosphate/$CaTiO_3$ composites were prepared by pressureless air sintering and characterized in terms of phase stability, microstructure and pole drilling for their suitability for machining. In hydroxylapatite/$CaTiO_3$ composites, Ti incorporation into the apatite structure caused lattice shrinkage and eventual decomposition of the hydroxylapatite associated with the formation of α-tricalcium phosphate during sintering at 1100 °C. Later, α-tricalcium phosphate disappeared at 1300 °C, possibly reacting with $CaTiO_3$ at the expense of both phases. On the other hand, tricalcium phosphate/$CaTiO_3$ composites were thermally stable up to 1100 °C insuring a weak interface between the components, which is one of the requirements for machinability in ceramic composites. Drilling tests also verified their suitability for machining.

Keywords: Hydroxylapatite; Tricalcium phosphate; $CaTiO_3$; Machinable ceramics

1. Introduction

Calcium phosphates have composition and structure similar to the mineral component of the calcified tissues (i.e., bones and teeth). Therefore, they are widely used in many orthopedic and dental implant systems in order to achieve fast chemical bonding between bone and implant [1,2]. Among various calcium phosphates, hydroxylapatite (HA), and tricalcium phosphates (TCP) have received most attention in scientific and industrial community. While pure 100% crystalline HA is known to be the most stable and the strongest calcium phosphate phase [3], TCP with a lower crystallinity introduces higher degradation rate in biological environment compared to crystalline HA [4].

For the implant/prosthesis applications of bulk calcium phosphates, e.g., in the form of scaffolds, customized geometries are demanded for the best fit to the space in which the scaffolds will be implanted. Engineering of such geometries of bioceramic implants requires a control of complex internal and external geometries during fabrication [5]. There are many different techniques currently used in fabrication; such as, micro-milling [6], textile [7], and solid free form (SFF) fabrication, such as; fused deposition [8], selective laser sintering (SLS) [9], stereolithography (STL) [10], 3D printing (3DP) [11].

Machining is one of the low cost techniques for fabrication of such geometries. However, high brittleness of calcium phosphates, like most of other ceramic materials, considerably decreases their ability to be machined to appropriate sizes and shapes. One of the common approaches to improve the machinability of such brittle ceramics is to introduce a weak interface phase in the ceramic matrix [12] to facilitate crack deflection during machining, as observed in mica-containing glass–ceramic [13]. Boron nitride (BN), and as one of the rare earth phosphates, Lanthanum phosphate ($LaPO_4$) are effective ceramic interface materials [14].

In this direction, efforts have been made to develop TCP/$LaPO_4$ composites suitable for machining [15]. Although they showed comparable osteoblast cell attachment to pure HA and TCP, main question aroused about their long term performance due to emitted La ions that may cause toxic effects, known as La toxicity [16].

In recent years, calcium titanate ($CaTiO_3$) has gained much attention in biomedical researches. It has lower solubility than HA in low pH conditions which may be created by osteoclast bone resorption or due to an inflammatory response [17]. In addition, significant apatite growth on $CaTiO_3$ in simulated body fluid (SBF) has been observed, thus, providing promise for the formation of bone-like structures on its surface [18]. Further biological studies on $CaTiO_3$ showed that it has better

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osteoblast adhesion than both pure HA and Ti [19]. Our previous researches also showed that osteoblast cell adhesion performance triples in HA and TCP composites with $CaTiO_3$ over pure HA or TCP. Therefore, even $CaTiO_3$ itself may be regarded as a desirable interfacial bioceramic for orthopedic implant applications [20,21].

The aim of this study was to characterize HA/$CaTiO_3$, TCP/$CaTiO_3$ composites in order to evaluate their suitability for machining. In this respect, HA/$CaTiO_3$ and TCP/$CaTiO_3$ composites were prepared and sintered in air at 500, 700, 900, 1100 and 1300 °C for 2 h, then characterized by XRD, SEM and simple drilling operation.

2. Experimental methods

Pure HA and TCP were synthesized by the precipitation method [3,15]. In order to prepare the composites, the synthesized powders were mixed with $CaTiO_3$ (Aldrich) in the appropriate weight ratios (Table 1). For homogeneous mixing, the powders were blended with ball milling in an ethyl alcohol medium. The milled powder was then quickly filtered through a 0.2 μm Millipore filter to prevent segregation due to density differences between the two types of powders. The filtered cakes were kept at 200 °C overnight to remove the rest of the ethyl alcohol used in the washings, then crushed and further mixed using a pestle and mortar.

The resulting powders of each different sample were cold pressed into pellets at 200 MPa. Subsequently, pellets were pressureless sintered at 500, 700, 900, 1100 or 1300 °C for 2 h in air. XRD analyses were performed with a Philips type PW2273/20 diffractometer operating with Cu Kα radiation at 40 kV and 35 mA. XRD spectra were collected at the diffraction angles (2θ) between 20° and 70° with 0.02°/min scan speed.

The structure of HA is usually considered to be hexagonal, with space group $P63/m$. However, there is evidence for monoclinic HA structure with atomic positions close to those of the hexagonal structure. The structure of HA was considered to be hexagonal for lattice parameter measurements. The volume (V) of a hexagonal unit cell was determined for each HA from the formula $V = 2.589a^2c$.

SEM micrographs were taken with Philips/FEI XL30FEG SEM. The machinability of specimen was tested using HSS drills operating at 2500 rpm [12,15].

Table 1
Abbreviation and composition of the compacts tested.

Compact	Abbreviation	Composition
Hydroxylapatite	HA	Pure
Tricalcium phosphate	TCP	Pure
Calcium titanate	$CaTiO_3$	100%
Hydroxylapatite/calcium titanate composites	HC30	70 wt.% HA + 30 wt.% $CaTiO_3$
	HC50	50 wt.% HA + 50 wt.% $CaTiO_3$
Tricalcium phosphate/calcium titanate composites	TC30	70 wt.% TCP + 30 wt.% $CaTiO_3$
	TC50	50 wt.% TCP + 50 wt.% $CaTiO_3$

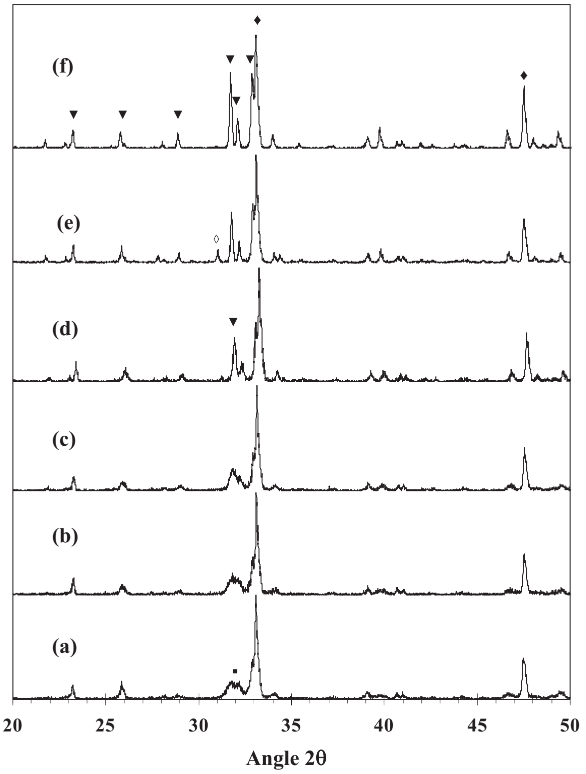

Fig. 1. XRD patterns of HC50 samples: (a) as synthesized; and air-sintered for 2 h at; (b) 500 °C; (c) 700 °C; (d) 900 °C; (e) 1100 °C; (f) 1300 °C (■: precipitated HA; ▼: crystallized HA; ◇: α-TCP; ◆: $CaTiO_3$). Y-axis = arbitrary units.

3. Results and discussion

XRD patterns of HA50 are shown in Fig. 1. It was observed that HA crystallized at temperatures between 700 and 900 °C. Small amount of α-TCP was observed in the samples sintered at 1100 °C, which was most probably due to a slight dissociation of HA. However, this phase disappeared upon sintering at 1300 °C. The intensity ratios of the characteristic peaks of $CaTiO_3$ to HA in HC30 at 1100 and 1300 °C were 0.75 and 0.68, respectively (XRD data is not given). These values for HC50 at 1100 and 1300 °C were 2.14 and 1.5. So the decreasing amount of $CaTiO_3$ relative to HA, associating with the disappearance of α-TCP, suggests that $CaTiO_3$ is also involved in this reaction, which resulted at expenses of both $CaTiO_3$ and α-TCP.

XRD patterns of TC50 are shown in Fig. 2. The precipitated HA started to transform into β-TCP upon sintering in between 500 and 700 °C, in a similar way reported in Ref [15]. HA totally disappeared at 900 °C and the only stable calcium phosphate phase was β-TCP at 900 and 1100 °C. On the other hand, α-TCP appeared upon sintering at 1300 °C, beside β-TCP, as the other stable calcium phosphate phase associated with $CaTiO_3$.

The calculated lattice parameters "a" and "c" in HA phase in HC composites are given in Table 2. In both cases, the lattice parameters in hexagonal structures were smaller than those of pure HA. This implies that the HA lattice shrank in volume with increasing amount of Ti ion uptake in an agreement with Ref. [22]. It may not be surprising since the ionic radius of Ti is smaller than that of all ions of pure HA: Ca, O, and P. The smaller radii of Ti ions incorporating in the HA's structure may

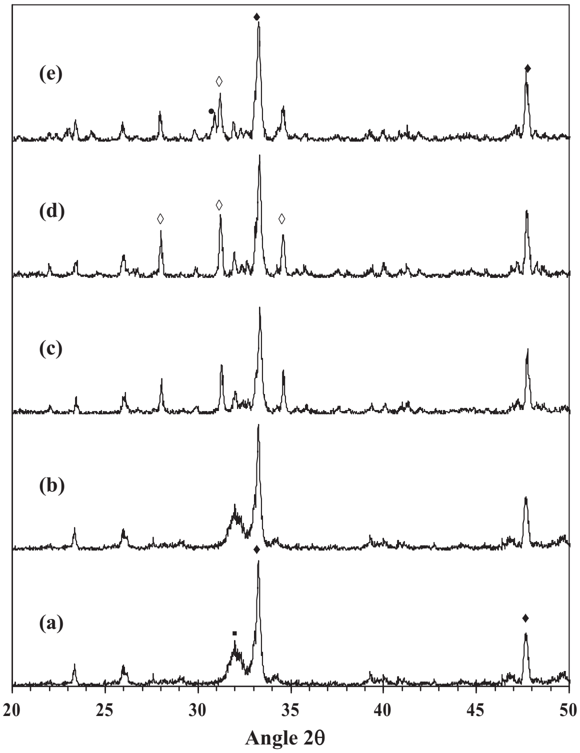

Fig. 2. XRD patterns of TC50: air-sintered for 2 h at; (a) 500 °C; (b) 700 °C; (c) 900 °C; (d) 1100 °C; (f) 1300 °C (■: precipitated HA; ▼: crystallized HA; ◇: β-TCP; ◆: calcium titanate, ●: α-TCP). *Y*-axis = arbitrary units.

introduce lattice disorder. It may be this induced lattice disorder provoking microscopic stresses in HA matrix, consequently lowering the required energy for the dehydration and causing respected decomposition upon sintering at 1100 °C [23]. As a result of the decomposition and reactions observed in HC composites during sintering, HA/$CaTiO_3$ composites are not stable and cannot fulfill the requirement necessary for machinability. It should also be emphasized that Ti ions seem to play a role in the stabilizing α-TCP in HC and TC composites upon sintering at 1100 °C.

In contrast, TC composites showed no reaction between $CaTiO_3$ and TCP phases upon sintering at 1100 °C and both phases stayed stable (Fig. 2), thus fulfilled one of the major requirements for machinability in composites [12]. The uniform distribution of $CaTiO_3$ in the composites can be seen in Fig. 3. Therefore, they can be considered to be suitable composites for machining when sintered at 1100 °C.

Table 2
Lattice parameters and lattice volumes of HA phase in composites.

Sample	Temp.	*a*	Δ*a*	*c*	Δ*c*	Δ*V*%
HA		9.427	0	6.888	0	0
HA in HC30	900 °C	9.411	−0.016	6.878	−0.013	0.48
	1100 °C	9.419	−0.008	6.889	−0.010	0.16
	1300 °C	9.411	−0.016	6.882	−0.001	0.43
HA in HC50	900 °C	9.411	−0.016	6.882	−0.006	0.43
	1100 °C	9.425	−0.002	6.881	−0.007	0.14
	1300 °C	9.408	−0.019	6.883	−0.005	0.48

Hexagonal lattice parameters *a* and *c* and differences Δ*a* and Δ*c*.

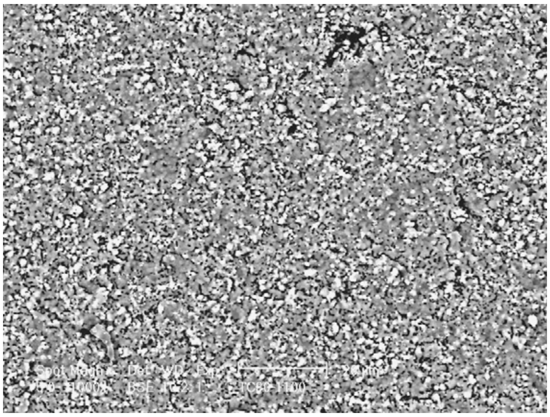

Fig. 3. SEM dark field image of TC50 composite sintered at 1100 °C in air for 2 h.

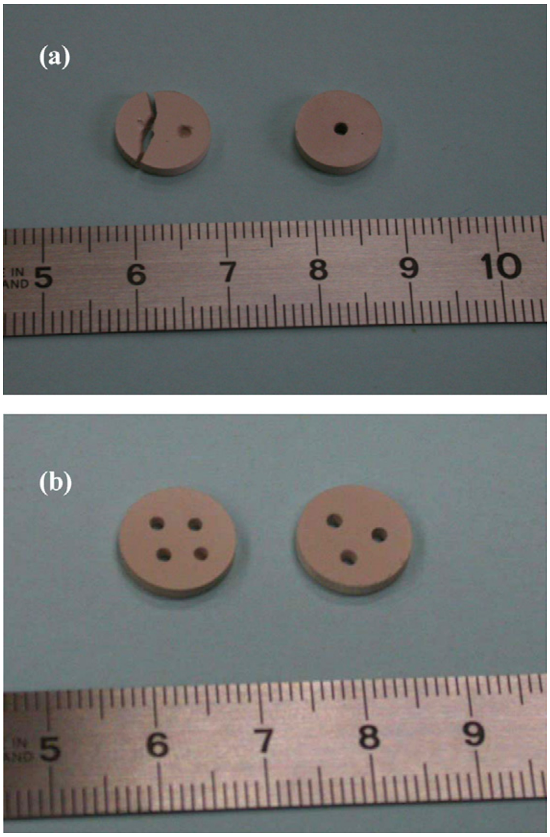

Fig. 4. Optical micrograph of machined composites using HSS drill: (a) TC30; (b) TC50 (units in cm).

Their suitability for machining was also tested with a simple drilling operation using HSS drills operating at 2500 rpm for verification. Some of the TC30 composites were broken during the drilling (Fig. 4(a)). This may be due to the dominance of the brittle nature of TCP associated with its larger amount in the composites. However, the composites TC50 did not break; well defined holes could be drilled (Fig. 4(b)).

From this perspective, this study demonstrated that $CaTiO_3$ addition into tricalcium phosphate can introduce a suitability for machining, which may be crucial for the fabrication of relatively complex shaped ceramic bone substitutes and implants for a large variety of clinical demands with relatively reduced costs compared to ceramic prototyping or other molding techniques. The weak bonding between tricalcium phosphate and $CaTiO_3$ seems to be responsible for this result. Keeping in mind the well-established biocompatibility of $CaTiO_3$, the results found in this study continues to provide support for $CaTiO_3$ in orthopedic applications [24].

4. Conclusions

Decomposition of hydroxylapatite and formation of α-tricalcium phosphate were observed in hydroxylapatite/$CaTiO_3$ composites during sintering above 900 °C. In addition, α-tricalcium phosphate and $CaTiO_3$ reacted upon sintering in between 1100 and 1300 °C. Thus, these composites did not show a thermal phase stability during sintering and, for this reason, do not have the properties required for machinability. On the other hand, no reaction was observed in tricalcium phosphate/$CaTiO_3$ composites and both tricalcium phosphate and $CaTiO_3$ phases stayed stable up to 1100 °C, forming weak interface which can provide an ability to be machined. Drilling tests also verified machining suitability.

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