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Reaction sintering of β-tricalcium phosphates and their mechanical properties

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Abstract

Various kinds of calcium oxides, carbonates and phosphates were used as the raw materials, and β-TCP ceramics was fabricated by reaction sintering at 1100 °C, and the sinterability, the reaction sintering behavior and mechanical properties of reaction-sintered β-TCP were investigated. Reaction-sintered bodies using $CaHPO_4$ + HAp consisted of single β-TCP phase, and bulk density and bending strength increased with extending sintering time. On the contrary, normal-sintered β-TCP synthesized using $CaHPO_4$ + HAp did not change in bulk density and bending strength with extending sintering time. Reaction-sintered body using $CaHPO_4$ + HAp as the raw materials showed higher bulk density and bending strength than normal sintered β-TCP.

Keywords: Sintering; Mechanical properties; Calcium phosphate

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1. Introduction

β-tricalcium phosphate (β-TCP) is one of the most attractive biomaterials for bone repair since it shows an excellent biological compatibility, osteoinductivity and safety in living tissues.[1–3] However, β-TCP shows lower mechanical strength and fracture toughness than natural bones. Several attempts for the improvement of mechanical properties of β-TCP have been made.

The present authors have paid attention to the structural characteristic of β-TCP, and synthesized β-TCP doped with various metal ions, and substitution model of monovalent, divalent and trivalent metal ions for β-TCP has been proposed.[4] Furthermore, its properties such as sinterability, mechanical properties, thermal stability were investigated.[5,6] It was found that the β-phase doped with metal ions would be stabilized at higher temperature than 1120–1180 °C (β-α phase transformation temperature reported by Monma et al.[7])[6], and the sinterability and bending strength of β-TCP could be improved by the formation of solid solution with sodium or magnesium ions.[5] Basically, β-TCP is used for bone substitute as porous materials and pore size of porous β-TCP should be controlled. In order to fabricate porous β-TCP with homogeneous pore size distribution and excellent mechanical strength, it is so important that the skeleton of porous β-TCP should be densified. However, β-α phase transformation occurs above 1120 °C and sintering temperature must be lower than the phase transformation temperature. Due to the limitation of sintering temperature, it is difficult to densify β-TCP and control the pore size distribution.

In order to further improve the sinterability and mechanical properties of β-TCP and simplify the fabrication of β-TCP sintered bodies, we tried to fabricate β-TCP ceramics by reaction sintering. Some studies on reaction sintering of the mixture of α- and β-TCP[8] and β-TCP/hydroxyapatite (HAp) composite[9] have been reported, but there were very few systematical reports on reaction sintering of β-TCP.

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In this study, various kinds of calcium oxides, carbonates and phosphates were used as the raw materials, and two kinds of them were selected, and we tried to fabricate β-TCP ceramics by reaction sintering. Furthermore, the sinterability of β-TCP by reaction sintering, their mechanical properties and reaction sintering behavior were investigated.

2. Experimental procedure

Various kinds of calcium oxides, carbonates and phosphates such as CaO, $Ca_{10}(PO_4)_6(OH)_2$ (HAp; Sangi, Saitama, Japan), $CaHPO_4$ (Kyowa Chemical Industry, Kagawa, Japan), $CaHPO_4{\bullet}2H_2O$ (Kishida Chemical, Osaka, Japan), $Ca_2P_2O_7$ and $CaCO_3$ (Kishida Chemical, Japan) were used as the raw materials. $Ca_2P_2O_7$ was synthesized via solid-state reaction using $CaCO_3 + CaHPO_4$, and CaO was prepared by pyrolysis of $CaCO_3$. Combinations and composition of these raw materials were shown in Table 1. The Ca/P molar ratio was 1.5, which is a stoichiometric composition of β-TCP. The raw materials were ball-milled for 48 h using ethanol as the solvent. After drying and crushing the powder by agate motor, the powder was formed into green compacts under a uniaxial pressure of 32 MPa, followed by cold isostatically pressed at 200 MPa. The compact was pressureless-sintered at 1100 °C for 24–48 h in air. We took β-α phase transformation temperature (1120–1180 °C[7]) and densification temperature into account, and selected the sintering temperature as 1100 °C. For comparison, β-TCP was synthesized via solid-state reaction using the same powder listed in Table 1, and the compact was formed, and then sintered under the same condition described above (normal sintering process). The sintered bodies were cut into rectangular bars ($3.0^t \times 4.0^w \times 34^l\ mm^3$).

Crystalline phase of the sintered bodies was identified using X-ray diffractometer with a rotating anode X-ray tube (XRD: RINT-1500, Rigaku, Tokyo, Japan). Bulk density was measured by Archimedes' method using ethanol as the solvent. Bending strength measurement was performed using a testing machine (AG-I, Shimadzu, Kyoto, Japan). Three-point bending strength was measured at room temperature in air with a crosshead speed of 0.5 mm/min and a lower span of 30 mm. The number of specimens for bending test was five. Fracture surface of β-TCP after bending test was observed by scanning electron microscope (SEM). Shrinkage process during sintering was evaluated by dilatometer (TD5000S, Bruker AXS, Tsukuba, Japan) from room temperature to 1100 °C at the heating rate of 3 °C/min in air.

Table 1
Combinations and composition of the raw materials for reaction sintering

	Combinations of the raw materials		Composition (wt%)	
	(a)	(b)	(a)	(b)
(1)	$CaHPO_4$	$CaCO_3$	73.1	26.9
(2)	$CaHPO_4$	$Ca_{10}(PO_4)_6(OH)_2$	21.3	78.7
(3)	$CaHPO_4{\bullet}2H_2O$	$Ca_{10}(PO_4)_6(OH)_2$	25.5	74.5
(4)	$Ca_2P_2O_7$	CaO	81.9	18.1
(5)	$Ca_2P_2O_7$	$Ca_{10}(PO_4)_6(OH)_2$	20.2	79.8

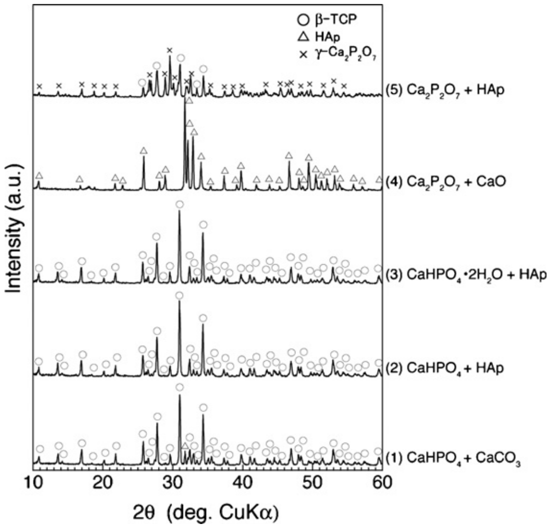

Fig. 1. X-ray diffraction patterns of reaction-sintered bodies using various combinations of the raw materials (sintering condition: 1100 °C, 24 h, in air).

3. Results and discussion

3.1. The effect of raw materials on crystalline phase, bulk density and bending strength of reaction-sintered bodies

X-ray diffraction patterns of reaction-sintered bodies using various combinations of the raw materials are shown in Fig. 1, and crystalline phase of each reaction-sintered body is shown in Table 2. In the case of the use of $Ca_2P_2O_7 + CaO$ as the raw materials, its reaction-sintered bodies mainly consisted of HAp. Reaction-sintered bodies using $CaHPO_4 + CaCO_3$ and $Ca_2P_2O_7 + HAp$ mainly consisted of β-TCP, but they contained HAp and $Ca_2P_2O_7$, respectively. On the other hand, reaction-sintered bodies using $CaHPO_4 + HAp$ and $CaHPO_4{\bullet}2H_2O + HAp$ consisted of single β-TCP phase.

Figs. 2 and 3 show bulk density and bending strength of sintered bodies obtained by reaction sintering at 1100 °C for 24 h using various combination of the raw materials, respectively. In the case of the use of $Ca_2P_2O_7 + CaO$ and $CaHPO_4 + CaCO_3$ as the raw materials, bulk density and bending strength of reaction-sintered bodies which contained HAp phase were very low, and the bulk density and bending strength were 1.70–1.80 g/cm^3 and 3–10 MPa, respectively.

From the results of bulk density and bending strength, it seemed reaction-sintered bodies containing β-TCP phase showed higher bulk density and bending strength. Reaction-sintered body using $CaHPO_4 + HAp$ as the raw materials which

Table 2
Crystalline phase of reaction-sintered bodies using various combination of the raw materials: (β-TCP:β-$Ca_3(PO_4)_2$, HAp:$Ca_{10}(PO_4)_6(OH)_2$)

	Raw materials	Crystalline phase
(1)	$CaHPO_4 + CaCO_3$	β-TCP, HAp
(2)	$CaHPO_4 + Ca_{10}(PO_4)_6(OH)_2$	β-TCP
(3)	$CaHPO_4{\bullet}2H_2O + Ca_{10}(PO_4)_6(OH)_2$	β-TCP
(4)	$Ca_2P_2O_7 + CaO$	HAp
(5)	$Ca_2P_2O_7 + Ca_{10}(PO_4)_6(OH)_2$	β-TCP, $Ca_2P_2O_7$

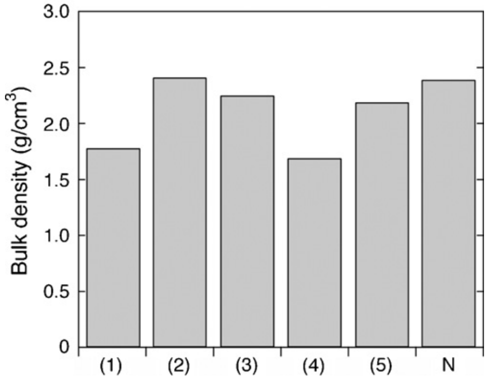

Fig. 2. Bulk density of reaction-sintered bodies using various combinations of the raw materials (sintering condition: 1100 °C, 24 h, in air). Each number in this figure corresponds to the number described in Table 1. For comparison, bulk density of normal-sintered body using β-TCP powder synthesized using $CaHPO_4$ + HAp were also shown in this figure (represented as "N").

consisted of single β-TCP phase showed higher bulk density and bending strength, and the values were 2.40 g/cm^3 (R.D.: 78%) and 36 MPa, respectively (the theoretical density of β-TCP[10] was assumed to be 3.07 g/cm^3). On the other hand, reaction-sintered body using $CaHPO_4{\bullet}2H_2O$ + HAp which also consisted of single β-TCP phase showed lower bending strength compared to reaction-sintered body using $CaHPO_4$ + HAp. This would be attributed to the decomposition of water contained in $CaHPO_4{\bullet}2H_2O$, resulting in decreasing bulk density and bending strength. For comparison, bulk density and bending strength of normal-sintered body using β-TCP powder synthesized using $CaHPO_4$ + HAp were also shown in Figs. 2 and 3, respectively. Bending strength of reaction-sintered body using $CaHPO_4$ + HAp was nearly the same as that of normal-sintered β-TCP synthesized using $CaHPO_4$ + HAp.

In consideration of these results, the use of $CaHPO_4$ + HAp as the raw materials would be effective to obtain the reaction-sintered β-TCP body with higher bulk density and bending strength.

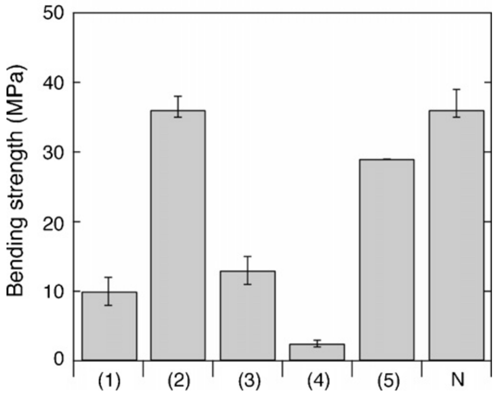

Fig. 3. Bending strength of reaction-sintered bodies using various combination of the raw materials (sintering condition: 1100 °C, 24 h, in air). Each number in this figure corresponds to the number described in Table 1. Error bars show the maximum and minimum values in each condition. For comparison, bending strength of normal-sintered body using β-TCP powder synthesized using $CaHPO_4$ + HAp was also shown in this figure (represented as "N").

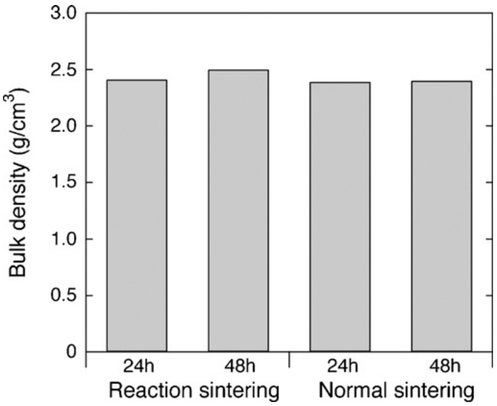

Fig. 4. The change in bulk density of reaction-sintered bodies using $CaHPO_4$ + HAp as the raw materials and normal-sintered β-TCP synthesized using $CaHPO_4$ + HAp with sintering time.

3.2. The effect of sintering time on bulk density and bending strength of reaction-sintered bodies

The effect of sintering time on bulk density and bending strength of reaction-sintered bodies using $CaHPO_4$ + HAp were evaluated. Figs. 4 and 5 show the change in bulk density and bending strength of reaction-sintered bodies using $CaHPO_4$ + HAp as the raw materials and normal-sintered β-TCP synthesized using $CaHPO_4$ + HAp with sintering time, respectively. In the case of reaction sintering, bulk density and bending strength increased with extending sintering time, and the vales were 2.40–2.50 g/cm^3 and 36–47 MPa, respectively. On the contrary, normal-sintered β-TCP synthesized using $CaHPO_4$ + HAp did not change in bulk density and bending strength with extending sintering time.

SEM micrographs of fracture surface of normal-sintered β-TCP synthesized using $CaHPO_4$ + HAp and reaction-sintered bodies using $CaHPO_4$ + HAp as the raw materials for 24–48 h are shown in Fig. 6. In the case of normal-sintered β-TCP, grain size did not change with extending sintering time, and sintering seemed to almost complete during heating at 1100 °C for

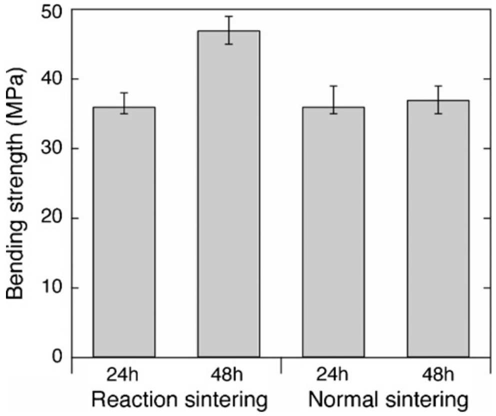

Fig. 5. The change in bending strength of reaction-sintered bodies using $CaHPO_4$ + HAp as the raw materials and normal-sintered β-TCP synthesized using $CaHPO_4$ + HAp with sintering time. Error bars show the maximum and minimum values in each condition.

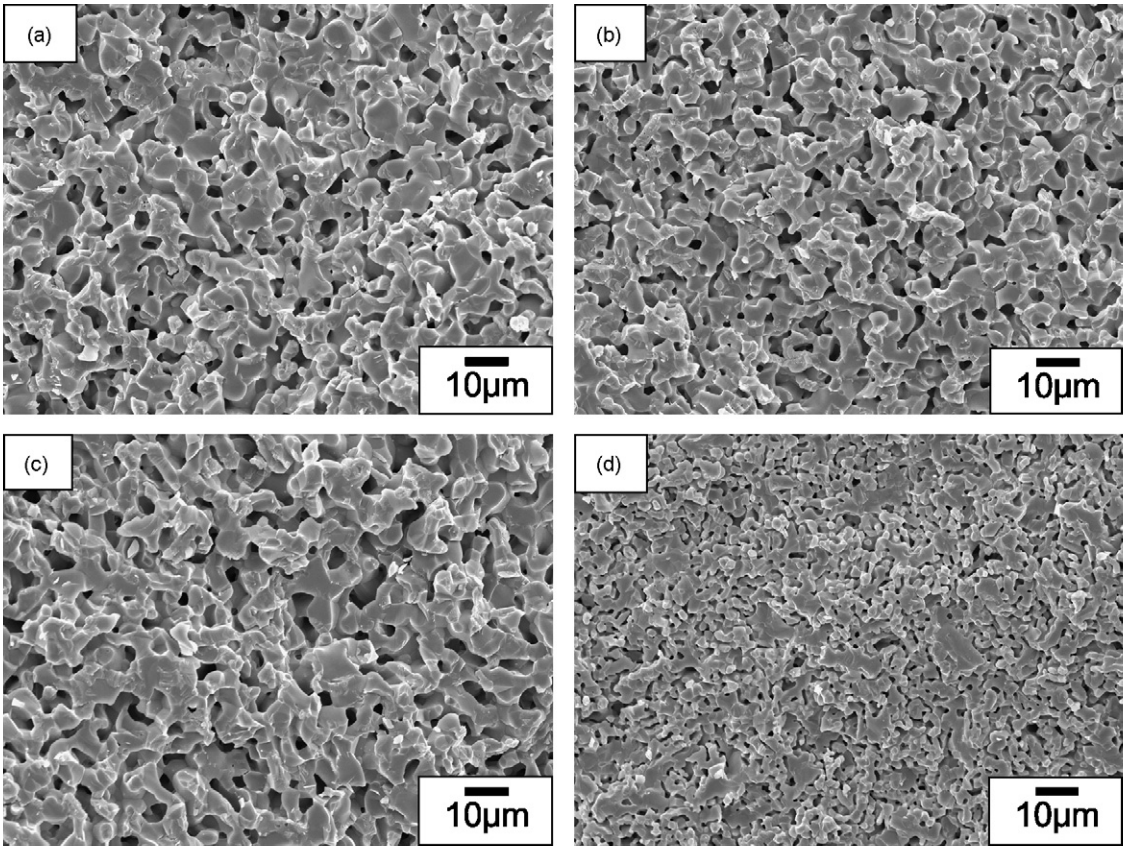

Fig. 6. SEM micrographs of fracture surface of normal-sintered β-TCP synthesized by the use of $CaHPO_4$ + HAp for (a) 24 h, (b) 48 h and reaction-sintered bodies using $CaHPO_4$ + HAp as the raw materials for (c) 24 h, (d) 48 h.

24 h. In the case of reaction sintering, reaction-sintered β-TCP for 24 h showed similar microstructure with normal-sintered β-TCP. As the sintering time extended to 48 h, sintering still proceeded and pore size and porosity decreased. These results corresponded to the change in bulk density and bending strength, i.e., reaction-sintered β-TCP exhibited higher bulk density and bending strength compared to normal-sintered β-TCP.

3.3. Reaction sintering behavior

Fig. 7 shows the shrinkage process of the compacts consisted of $CaHPO_4$ + HAp mixture and β-TCP powder synthesized using $CaHPO_4$ + HAp. The compact of β-TCP powder synthesized using $CaHPO_4$ + HAp started to shrink around 840 °C, whereas the compact consisted of $CaHPO_4$ + HAp mixture gradually shrank up to approximately 600 °C, and then showed significant shrinkage over 600 °C.

In order to investigate the reaction sintering behavior using $CaHPO_4$ + HAp, the compacts using $CaHPO_4$ + HAp were formed under the same condition described in experimental procedure, and crystalline phase of heat-treated body using $CaHPO_4$ + HAp at 600–1100 °C were evaluated. In addition, thermogravimetry and differential thermal analysis (TG–DTA; TG–DTA 2000S, Bruker AXS, Tsukuba, Japan) was also performed from room temperature to 1100 °C in air.

TG–DTA curves of $CaHPO_4$ + HAp mixture with the Ca/P molar ratio of 1.5 was shown in Fig. 8. Three steps of weight loss could be observed in TG. Reactions corresponding to each TG–DTA behavior was determined on the basis of XRD results and described below.

X-ray diffraction (XRD) patterns of reaction-sintered bodies using $CaHPO_4$ + HAp as the raw materials at various temperatures from 600 to 1100 °C in air were shown in Fig. 9. XRD patterns of reaction-sintered body at 600 and 700 °C showed diffraction peaks derived from HAp and γ-$Ca_2P_2O_7$, and γ-$Ca_2P_2O_7$ was formed by the decomposition of $CaHPO_4$. At 800 °C, diffraction peaks of HAp and γ-$Ca_2P_2O_7$ reduced and

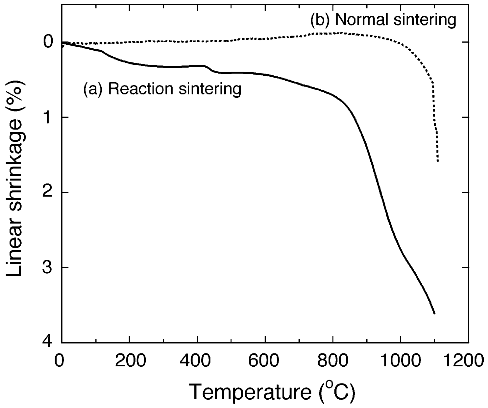

Fig. 7. Shrinkage process of the compacts consisted of (a) $CaHPO_4$ + HAp mixture (reaction sintering) and (b) β-TCP powder synthesized using $CaHPO_4$ + HAp (normal sintering).

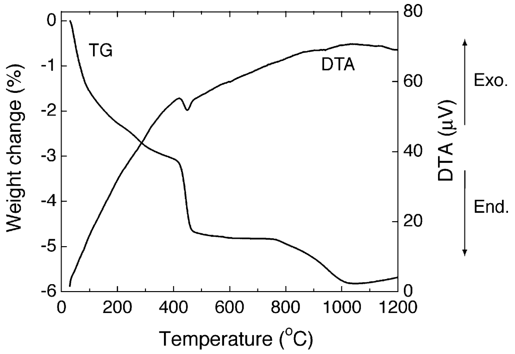

Fig. 8. TG–DTA curves of $CaHPO_4$ + HAp mixture with the Ca/P molar ratio of 1.5.

β-TCP phase appeared via solid-state reaction between HAp and γ-$Ca_2P_2O_7$. The reaction-sintered body at 900 °C mainly consisted of β-TCP phase, but small amount of HAp phase existed. XRD pattern indicated that the reaction-sintered body consisted of single β-TCP phase over 1000 °C.

In consideration of the results of XRD, each weight loss patterns in TG curve shown in Fig. 8 would correspond to the following reaction. First weight loss up to around 400 °C would be attributed to the desorption of adsorption water from the raw materials. Abrupt weight loss occurred and endothermic peak was observed at around 400 °C due to the pyrolysis of $CaHPO_4$:

$$2CaHPO_4 \rightarrow \gamma\text{-}Ca_2P_2O_7 + H_2O \qquad (1)$$

This reaction has been reported by Ropp et al.[11] and our results agreed with their report. Weight loss between 750 °C and 1000 °C would derive from the formation of β-TCP via the following reaction between HAp and γ-$Ca_2P_2O_7$, that has been already confirmed by Marraha et al.[12]:

$$Ca_{10}(PO_4)_6(OH)_2 + \gamma\text{-}Ca_2P_2O_7 \rightarrow 4\beta\text{-}Ca_3(PO_4)_2 + H_2O \qquad (2)$$

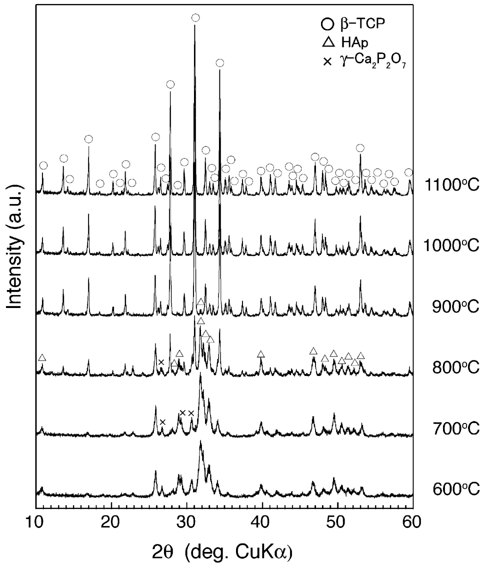

Fig. 9. X-ray diffraction patterns of reaction-sintered bodies using $CaHPO_4$ + HAp as the raw materials at various temperatures from 600 to 1100 °C in air.

From these results and shrinkage behavior, first small shrinkage up to around 600 °C in reaction sintering would indicate the volume change derived from the pyrolysis of $CaHPO_4$, and the significant shrinkage over 600 °C (especially over 800 °C) would be caused by the formation of β-TCP and progress in the sintering of β-TCP. These results suggested that reaction sintering of β-TCP using $CaHPO_4$ + HAp would proceed via following steps; (i) the shrinkage behavior of the raw materials, (ii) volume reduction caused via chemical reaction such as pyrolysis of $CaHPO_4$, (iii) mainly sintering of HAp phase, (iv) the formation of β-TCP, and then (v) sintering of β-TCP. Details of reaction-sintering mechanism are now under investigation.

From these results, we concluded that reaction sintering using $CaHPO_4$ + HAp as the raw materials would be effective for good sinterability, higher bulk density and bending strength. Further study on reaction-sintered β-TCP is now ongoing.

4. Conclusions

In this study, various kinds of calcium oxides, carbonates and phosphates were used as the raw materials, and two kinds of them were selected, and we tried to fabricate β-TCP ceramics by reaction sintering at 1100 °C, and the sinterability, reaction-sintering behavior and mechanical properties of reaction-sintered β-TCP were investigated.

Reaction-sintered bodies using $CaHPO_4$ + HAp and $CaHPO_4{}^\bullet 2H_2O$ + HAp consisted of single β-TCP phase, and bulk density and bending strength of reaction-sintered body using $CaHPO_4$ + HAp were higher than that of reaction-sintered body using $CaHPO_4{}^\bullet 2H_2O$ + HAp. Reaction-sintered body using $CaHPO_4$ + HAp as the raw materials showed higher bulk density than reaction-sintered bodies using the other raw materials. However, bending strength of reaction-sintered body using $CaHPO_4$ + HAp at 1100 °C for 24 h was nearly the same as that of normal-sintered β-TCP powder synthesized using $CaHPO_4$ + HAp.

In the case of normal-sintered β-TCP synthesized using $CaHPO_4$ + HAp, bulk density and bending strength slightly did not change with extending sintering time. On the other hand, bulk density and bending strength of reaction-sintered β-TCP increased with extending sintering time, and the values were higher than that of normal-sintered β-TCP.

From the results of TG–DTA analysis, XRD analysis and shrinkage behavior, reaction sintering of β-TCP using $CaHPO_4$ + HAp would proceed via following steps; (i) the shrinkage behavior of the raw materials, (ii) volume reduction caused via chemical reaction such as pyrolysis of $CaHPO_4$, (iii) mainly sintering of HAp phase, (iv) the formation of β-TCP, and then (v) sintering of β-TCP. From the results, it was found that reaction sintering using $CaHPO_4$ + HAp as the raw materials would be effective for good sinterability, higher bulk density and bending strength.

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