

## Fabrication of Nano-Sized $\beta$ -TCP Powder by an Organic-Inorganic Solution Route

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Highly sinterable, nano-sized  $\beta$ -tricalcium phosphate (TCP) powder was fabricated by an organic-inorganic solution route. Calcium nitrate and phosphoric acid were dissolved in D.I. water and 5 wt% polyvinyl alcohol (PVA) solution was added. The PVA was used as an organic carrier for the precursor gel. The dried precursor gel was fully crystallized to  $\beta$ -TCP at 1000 °C in an air atmosphere. As well, in the calcination process, the  $\text{NO}_x$  and  $\text{CO}_2$  gases from the calcium nitrate and PVA polymer made the precursor gel to a soft and porous powder. The synthesized  $\beta$ -TCP powder was agglomerated showing nano-sized primary particles. The ball-milled and compacted  $\beta$ -TCP powder was fully densified at 1200 °C for 1 h. In particular, the sintered  $\beta$ -TCP showed pure  $\beta$  phase without phase transformation to  $\alpha$ . In this process, the Ca/P ratio for stoichiometric  $\beta$ -TCP was adjusted by the control of phosphoric acid content.

**Key words:** Beta-TCP, Polymer, Synthesis, Powder, Microstructure.

### Introduction

Bone substitutes need to be biocompatible and have to be integrated by the surrounding bone tissue. It is generally acknowledged that calcium phosphate ceramics like hydroxyapatite (HAp) and tricalcium phosphate (TCP) are a good candidate for bone substitutes due to their chemical similarity to bone mineral [1-3]. In particular, bioresorbable  $\beta$ -TCP can be used for transient, clean and effective scaffold for bone reconstruction [4]. The HAp and TCP have been synthesized by wet-chemical methods. However, the methods resulted in the formation of non-stoichiometric powders [5, 6]. In particular, TCP has also little non-stoichiometry [4]. So, in the Ca/P ratio range of out of stoichiometry, TCP and a little  $\text{Ca}_2\text{P}_2\text{O}_7$  can exist according to phase diagram  $\text{CaO-P}_2\text{O}_5$ .

To use  $\beta$ -TCP ceramics as surgical implants, the mechanical strength of  $\beta$ -TCP ceramics must be as high as possible. So, it is important to densify  $\beta$ -TCP ceramics intensively. In general, it is difficult to sinter  $\beta$ -TCP ceramics fully because  $\beta$ -TCP ceramics should be sintered at lower temperature than that of phase transition to  $\alpha$ -TCP, 1180 °C. Actually, fully densified  $\beta$ -TCP was not obtained at below 1200 °C in any report so far. The  $\beta$  to  $\alpha$  transformation of TCP can be affected by departure from the stoichiometric Ca/P molar

ratio (1.50). M. Bohner et al. reported that little conversion into  $\alpha$ -TCP was obtained in the  $\beta$ -TCP with low Ca/P ratio (1.47) at 1300 °C [7].

Chemical processing routes based on organic/inorganic complexation in solution have recently been used to produce pure and homogeneous ceramic powders [8]. In the process, the polymeric long chain in the mixture ensures the homogeneous distribution of the metal ions in its polymeric network structure and inhibits their segregation and/or precipitation from the solution. Polyvinyl alcohol (PVA) is one of the polymeric carriers for the polymer complexation process [8]. The polymer surrounds and covers the cations or sol particles, which decreases their mobility and constrains the system to reduce premature agglomeration. The process also produces porous and carbonaceous materials that give heat through its combustion, so that soft, fine and single-phase powders can be formed at a relatively low external temperature [8-10].

In this work, the  $\beta$ -TCP powder is synthesized by a new wet-chemical method using a PVA as an organic carrier. The effects of mixing ratio of calcium metal salt and phosphoric acid on the synthesis behavior are examined. In addition, the sintering behavior of  $\beta$ -TCP powder is examined with the synthesized and ball-milled, nano-sized powder to obtain fully densified  $\beta$ -TCP ceramics.

### Experiment Procedure

#### Powder synthesis

Calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , reagent grade, Aldrich

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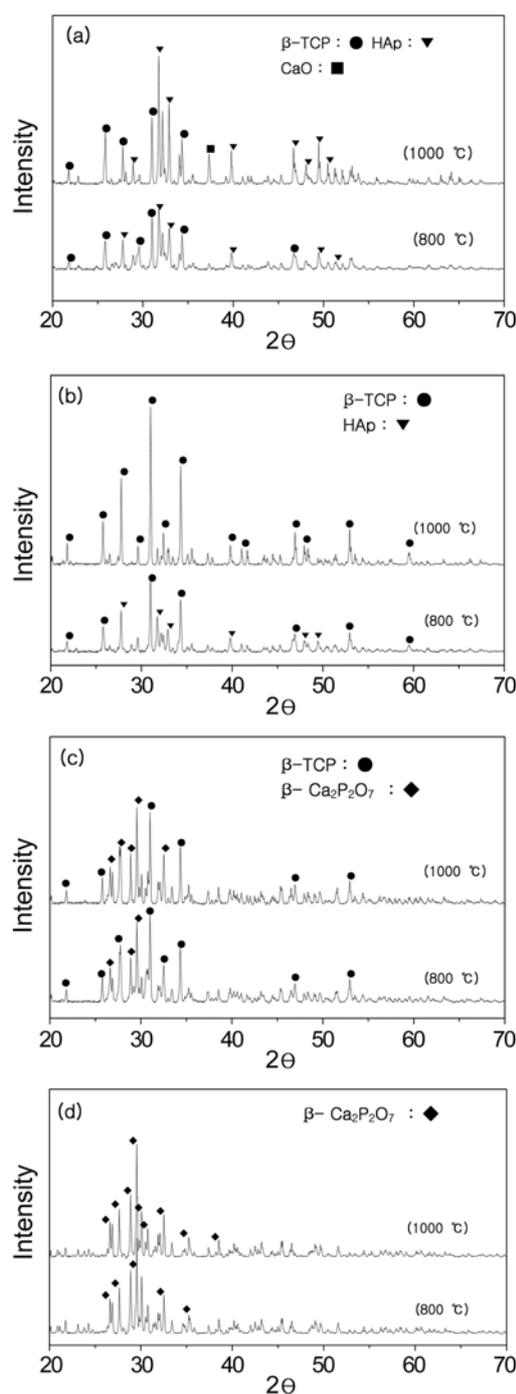
Chem. Co., Milwaukee, WI) and phosphoric acid ( $\text{H}_3\text{PO}_4$ , reagent grade, Duksan Co., Ansan, Korea) were dissolved in various proportions in deionized (DI) water. Once the cation sources were completely dissolved, the 5 wt% PVA (Air Products and Chemicals, Inc., Airvol Series, Allentown, PA) was dissolved in DI water and added. The PVA, which has a D.P. (degree of polymerization) value of 1625 (monomers/polymer) and a molecular weight of 153,000, was used for the preparation of precursor. The proportions of the PVA to cation sources in the solution were adjusted in such a way that there was 4 times more positively charged valences from the cations than from the potentially negatively charged (OH) functional groups of the polymers. The polymeric long chains have hydroxyl groups in solution. Hence, one PVA monomer, which has one hydroxyl (OH) functional group, can be used as an unit for calculation of PVA content. The exact relative amount of PVA to cations in the solution can be calculated with reference to a monomeric unit of PVA. Water evaporated by continuous stirring during heating on a hot plate. The resulting gel-type precursor was completely dried for several hours at  $100^\circ\text{C}$ . The organic/inorganic precursors were then ground and kept in a desiccator because of their hydrophilic characteristics. Each of the ground precursors were calcined or crystallized at various temperatures in an air atmosphere in a box furnace. The calcined  $\beta$ -TCP powder was ball milled for 12 h. The charge included 20 g powder with zirconia ball media having ball diameters of 5 mm. The jar volume was 250 ml and 100 ml isopropyl alcohol was used for wet milling. The ball milled and dried powders were uni-axially pressed at 20 MPa. The pellet-shaped, green compacts were sintered, and then characterized.

### Characterization

Development of crystalline phases of the dried gels was studied, as functions of mixing ratio and heating temperature, using a X-ray diffractometer (Rigaku D/Max 2200) with  $\text{CuK}_\alpha$  radiation (40 kV, 30 mA). The measurements were made with a scanning speed of  $8^\circ/\text{min}$  and a sampling interval of  $0.02^\circ$ , over a range of  $20$ – $70^\circ$  at room temperature. The morphological characteristics of the synthesized  $\beta$ -TCP powders pre and after ball-milling, and sintered samples were examined by scanning electron microscopy (SEM, Hitachi, S-3500N). The nano-sized primary particles in the ball-milled powder were examined by transmission electron microscopy (TEM, Hitachi H-600). The Ca/P molar ratios at each wt% mixing ratio were examined by chemical analysis using ICP AES (Spectroflame EOF) with the synthesized powders.

### Results and Discussion

The organic-inorganic precursors resembled an aerogel and the porous powders were formed by the develop-



**Fig. 1.** XRD patterns of precursors, calcined at  $800^\circ\text{C}$  and  $1000^\circ\text{C}$  for 1 h, derived from (a) stoichiometric proportion for  $\beta$ -TCP, and (b) 20 wt%, (c) 50 wt% and (d) 100 wt% excess content of phosphoric acid.

ment of foam during the solution drying process. The foam was generated during evolution of  $\text{NO}_x$  gases caused by the decomposition of the calcium nitrate. The expansion of the gel due to the evolving  $\text{NO}_x$  gases continued until the precursors dried completely.

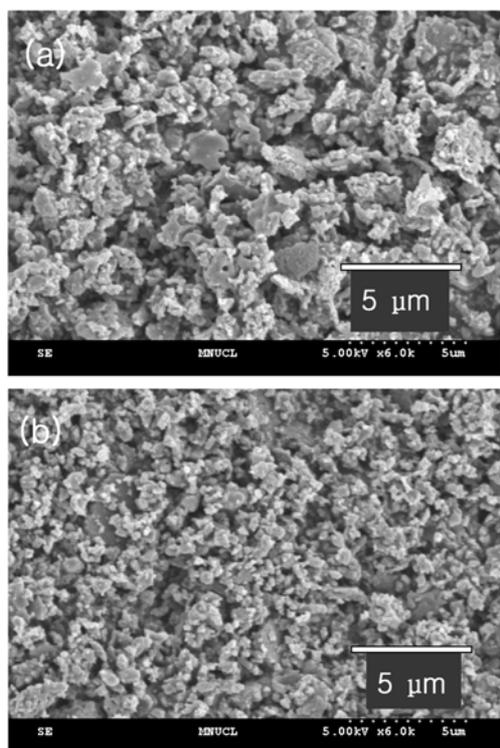
The XRD patterns of the calcium phosphate powders according to the mixing ratio and calcination temperature are presented in Fig. 1. HAp and  $\beta$ -TCP were

**Table 1.** Ca/P molar ratios at each phosphoric acid content

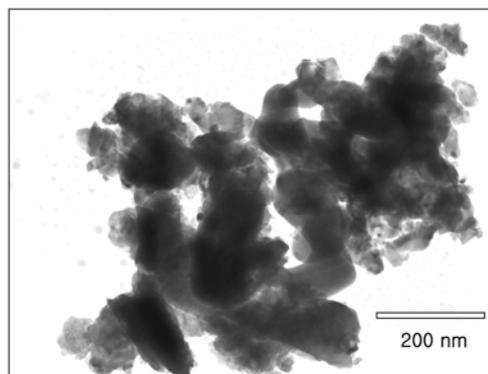
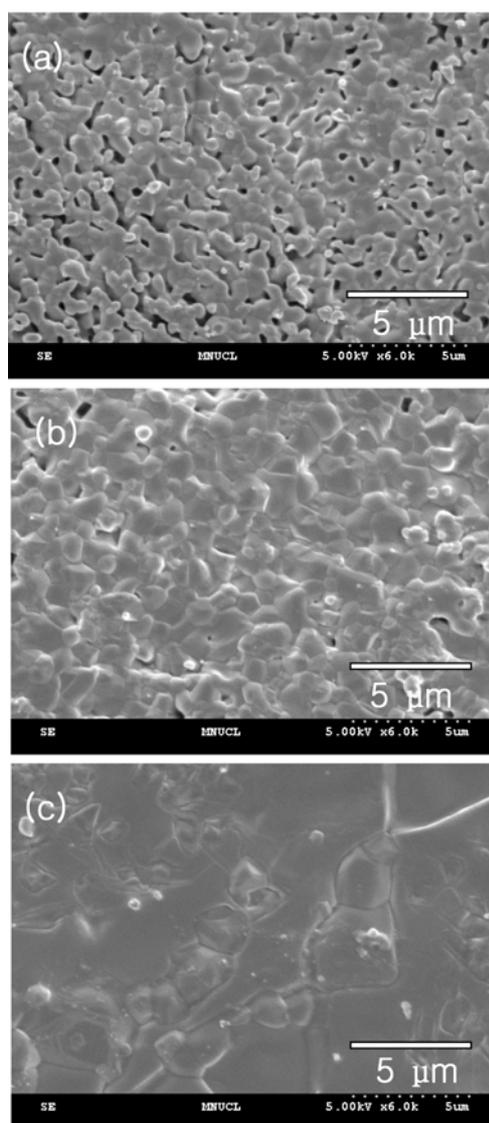
Phosphoric acid content	Ca/P ratio
stoichiometric	1.68
20 wt% excess	1.57
50 wt% excess	1.41
100 wt% excess	1.28

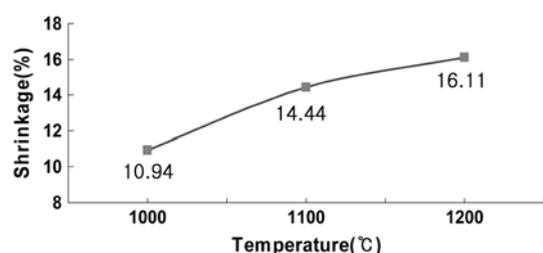
synthesized in the stoichiometric mixing proportion as shown in Fig. 1(a), and un-reacted CaO was observed at 1000 °C. These results mean that the amount of phosphoric acid changes from the initial wt% mixing ratio because some portion of phosphoric acid evaporates during the drying process. So, an excess phosphoric acid is necessary for the synthesis of phase-pure  $\beta$ -TCP. The  $\beta$ -TCP phase was observed in the wide mixing ratio, however, the fully crystallized  $\beta$ -TCP was observed in the 20 wt% excess content of phosphoric acid at 1000 °C. In the 50 wt% excess content,  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phase was observed with  $\beta$ -TCP. In the two times more phosphoric acid, only  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phase was observed as shown in Fig. 1(d).

The Ca/P molar ratios at each mixing ratio are listed in Table 1. The Ca/P ratios were determined with the powders crystallized at 1000 °C. In this study, the Ca/P ratio of stoichiometric  $\beta$ -TCP (1.50) was observed in the range of 20 wt% to 50 wt% excess content of phosphoric acid. The Ca/P ratio was closer to stoichiometry in the 20 wt% excess content and fully crystallized  $\beta$ -TCP was observed in this condition.

**Fig. 2.** SEM morphologies of (a) synthesized  $\beta$ -TCP powder (20 wt% excess) at 1000 °C for 1 h and (b) ball-milled  $\beta$ -TCP powder.

The morphologies of the synthesized  $\beta$ -TCP and ball-milled powders are shown in Fig. 2. The soft agglomerated powder (Fig. 2(a)) was easily ground by simple ball milling process. The SEM micrograph of

**Fig. 3.** TEM micrograph of ball-milled  $\beta$ -TCP powder.**Fig. 4.** SEM micrographs of sintered  $\beta$ -TCP at (a) 1000 °C (b) 1100 °C and (c) 1200 °C for 1 h.



**Fig. 5.** Shrinkage behavior of the sintered  $\beta$ -TCP at various temperatures.

the ball-milled  $\beta$ -TCP powder (Fig. 2(b)) was ultra-fine and agglomerated. The ball-milled powder was also examined by TEM and the result is presented in Fig. 3. Nano-sized primary particles were observed, however, the size was not uniform.

The SEM micrographs of the sintered  $\beta$ -TCP and shrinkage behavior at each sintering temperature are presented in Figs. 4 and 5. The powder compacts made from ball-milled  $\beta$ -TCP were densified showing about 16% shrinkage at 1200 °C for 1 h. An abnormal grain growth was observed at 1200 °C and the powder compact was nearly full-densified showing an irregular grain size. The fully densified  $\beta$ -TCP showed only  $\beta$  phase in XRD analysis without any  $\alpha$  phase. The  $\beta$  phase of the sintered sample at 1200 °C can be explained by the little conversion into  $\alpha$ -TCP caused by Ca/P ratio of out of stoichiometry according to the reference [7].

### Conclusions

$\beta$ -TCP powders were successfully synthesized by organic-inorganic solution technique employing PVA polymer as an organic carrier. In this process, the loss

of phosphoric acid during synthesis process could be adjusted by the addition of excess phosphoric acid, and the closer Ca/P ratio for stoichiometry was obtained in the 20 wt% excess content. Ball-milled  $\beta$ -TCP powder having nano-sized primary particles, was fully densified without phase transformation by sintering at 1200 °C for 1 h. In particular, abnormal grain growth was observed above 1100 °C.

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