

# Preparation of $\beta$ -TCP with high thermal stability by solid reaction route

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Starting from commercial materials,  $\beta$ -TCP powder was prepared by a conventional solid reaction route. Using DTG, TG and DTA, the mass change and the heat flow during heating of the commercial powder mixture were tested. The phase evolution at each step of the heating was monitored using XRD analyses. Based on the tests and the analyses the reaction details were analyzed. The  $\beta$ -TCP powder prepared in this study has high thermal stability. The phase transition temperature from  $\beta$  to  $\alpha$  was determined to be 1350°C, 200°C higher than commercial  $\beta$ -TCP powder (Plasma Biotol). The high phase transition temperature was due to Mg trace in the starting materials. © 2003 Kluwer Academic Publishers

## 1. Introduction

Calcium phosphate bioceramic materials are clinically used for bone substitution applications by virtue of their chemical and structural similarity to the mineral phase of bone and tooth [1, 2]. Hydroxyapatite (HAP),  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , and  $\beta$ -tricalcium phosphate ( $\beta$ -TCP)  $\text{Ca}_3(\text{PO}_4)_2$  are two important members of this family of compounds [3]. It is well evidenced that sintered HAP and TCP exhibit good biocompatibility.  $\beta$ -TCP and HAP implants become surrounded by new bone within a few weeks after implantation at bony sites [4]. Studies have further shown that HAP behaves as an inert implant, while  $\beta$ -TCP as a mildly bioresorbable one. High temperature phase of calcium phosphate, namely  $\alpha$ -TCP, absorbs proteins from living body liquid too fast to be suitable for bone implantation [5]. Different phases of calcium phosphate exhibit variable solubility with protein:  $\text{HA} < \beta\text{-TCP} < \alpha\text{-TCP}$ .

At high temperature HAP transforms into  $\beta$ -TCP although the transformation can be reversible. As the temperature is further increased up to  $1150 \pm 10^\circ\text{C}$ ,  $\beta$ -TCP changes to be  $\alpha$ -TCP automatically but non-reversibly. Then  $\alpha$ -TCP can then be retained to room temperature [6]. The intrinsic problem of the artificial bone made from HAP and  $\beta$ -TCP is their low mechanical strengths. Perfect sintering of  $\beta$ -TCP is necessary but is usually limited by the  $\beta$ - $\alpha$  transformation temperature (1140–1160°C). It is thus of significance to increase the phase transformation temperature, i.e. to enhance high temperature stability, by means of any conventional materials scientific methods. One of the approaches to enhancing the mechanical properties of artificial bones is to incorporate  $\beta$ -TCP into high performance and bioin-

ert ceramics, e.g. alumina. The preparation of the composites can be accomplished by fast sintering e.g. spark plasma sintering, during which densification is accomplished in few minutes or even seconds so that the reaction of  $\beta$ -TCP and alumina could be avoided. The high temperature stability of  $\beta$ -TCP in composites determines the quality of the artificial bone.

In this paper, the preparation of pure  $\beta$ -TCP powder with a high phase transformation temperature by the conventional solid reaction method is introduced. The solid reaction process towards  $\beta$ -TCP was investigated by using thermal gravimetric and differential thermal analyses as well as X-ray diffraction phase analyses. On the basis of the investigations, reactions in each step of the whole solid reaction process are analyzed. Pure  $\beta$ -TCP powder was prepared and the phase transformation temperature was found to be 1350°C, much higher than that of a commercial  $\beta$ -TCP (Plasma Biotol).

## 2. Experimental

In this study,  $\beta$ -TCP was synthesized by solid reaction of calcium carbonate with dibasic ammonium phosphate. The starting materials were calcium carbonate ( $\text{CaCO}_3$  extra pure-reagent grade, but 0.6% magnesium contained) and dibasic ammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ , extra pure reagent-grade) all provided by Shimakyo Chemical, Japan. The as-received powders were pulverized individually, and then mixed with the Ca/P molar ratio of 1.5 by ball milling. The ball milling process was conventionally performed using alumina balls as the medium and ethyl alcohol as the solvent. The weight ratio of powder, medium

and solvent was 8:14:8 and the milling time was about 24 hours. The slurry was filtered through a 100 mesh screen and dried in a rotatory evaporator. The dried lump was moved to an isothermal oven soaking at 105°C for 24 hours. The uniform mixture of CaCO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> powders was finally obtained by smashing the dry lumps and sieving through 200 meshes.

In order to investigate the solid reaction steps towards β-TCP, the powder mixture contained in an alumina crucible was first moved to the chamber of the thermal gravimetric analyzer (Thermal Gravimetric Analysis, TGA/Differential Thermal Analysis, DTA, Setaram, TGA24). The DTG (differential thermal gravity analysis), TGA (thermal gravity analysis) and DTA (differential thermal analysis) were performed simultaneously at a heating rate of 10°C/min. up to 1300°C. Weight lose and heat flow curves including exothermic and endothermic peaks over the temperature range were recorded. At each intermediate temperature between two neighboring peaks on the DTG curve the powder mixtures were isothermally heat-treated for three hours, respectively. After that phases of each sample were examined using X-ray diffraction (XRD) method (Rigaku D/max-II B). By combining DTG, TGA, DTA curves and XRD results, the solid reaction steps were analyzed and the possible reactions in each step were proposed.

On the basis of above investigation, β-TCP powder was prepared by heating the powder mixture at 6°C/min up to 1200°C and held at this temperature for 5 hours. The loose and porous product was then

pulverized and screened through 325 meshes. Phase analysis by XRD showed that the resultant powder was the single phase of β-TCP. In order to study the thermal stability, isothermal heat treatments for 5 hours at temperatures 1250°C, 1300°C, 1350°C and 1400°C were conducted on the as-prepared β-TCP powder followed by XRD analyses. The lattice constants of β-TCP powders were estimated. The thermal stability mainly with β-α transition temperature concerned was studied. For comparison, parallel analyses were also done on a commercial β-TCP powder (Plasma Biotol Limited, UK). The as-prepared β-TCP powder was also observed under scanning electron microscopy (SEM).

### 3. Results and discussion

The mixture of CaCO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Ca/P = 1.5) was heated at 10°C/min up to 1300°C in the thermal gravimetric analyzer. Figs 1 and 2 are the results of DTG and TG of the mixture obtained during the above course. In a narrow range of 200–230°C the weight of the mixture was lost by 13%, and the fastest weight loss occurred at 211°C. Consecutive weight losses of 5.2% and 6.3% were observed in the following temperature ranges of 430–505°C and 755–795°C, respectively. The corresponding fastest weight loss temperatures were 483°C and 773°C. Fig. 3 is the DTA curve of the mixture recorded simultaneously with DTG and TG. Exothermic peak at 211°C, the same temperature where first DTG peak appeared, was also found. As the temperature went above 250°C, the curve switches to

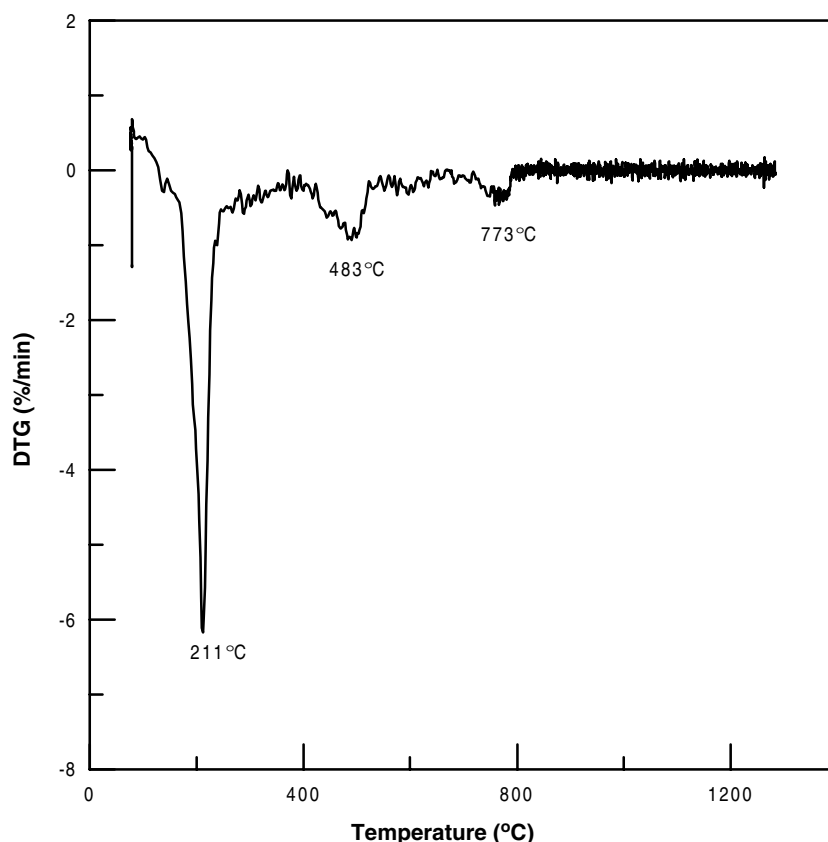


Figure 1 Differential gravimetric analysis of CaCO<sub>3</sub>/(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> mixture.

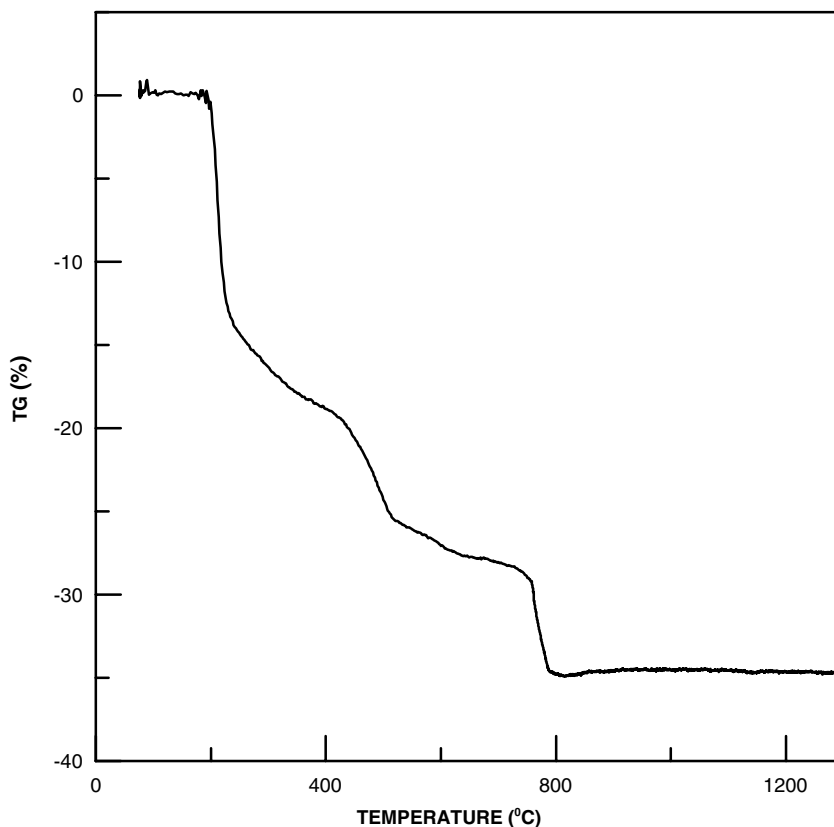


Figure 2 Thermal gravimetric analysis of  $\text{CaCO}_3/(\text{NH}_4)_2\text{HPO}_4$  mixture.

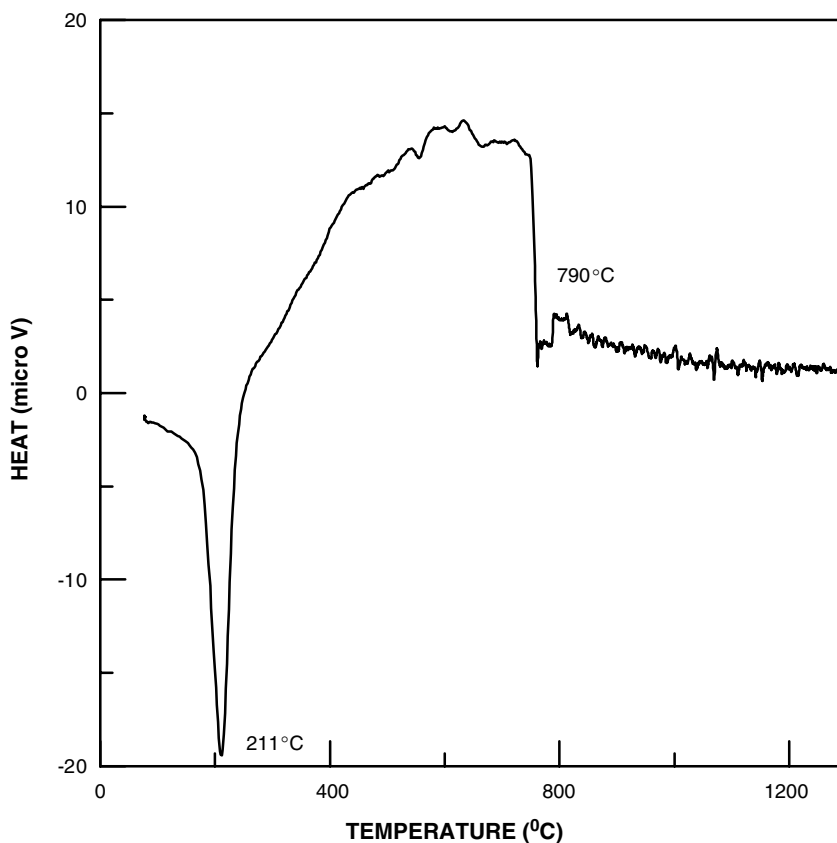


Figure 3 Differential thermal analysis of  $\text{CaCO}_3/(\text{NH}_4)_2\text{HPO}_4$  mixture.

exothermic until  $800^\circ\text{C}$  and all events accompanying the weight losses shown in Figs 1 and 2 merged as a whole in the DTA curve. It is worthy of note that nothing continued to take place as the temperature was above  $800^\circ\text{C}$ .

Fig. 4 summarizes the XRD patterns of as-mixed and isothermally heat-treated mixtures of  $\text{CaCO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  ( $\text{Ca}/\text{P} = 1.5$ ). The heat treatment time was 3 hours and the temperatures were  $300^\circ\text{C}$ ,  $600^\circ\text{C}$ ,  $780^\circ\text{C}$  and  $800^\circ\text{C}$ , respectively. These temperatures

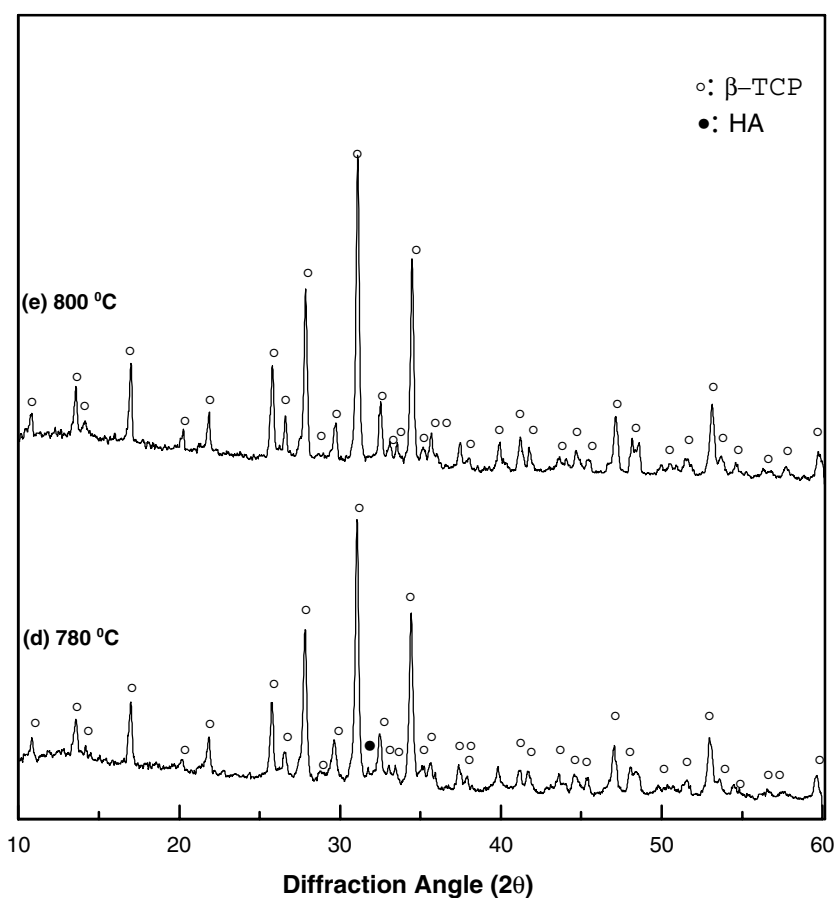
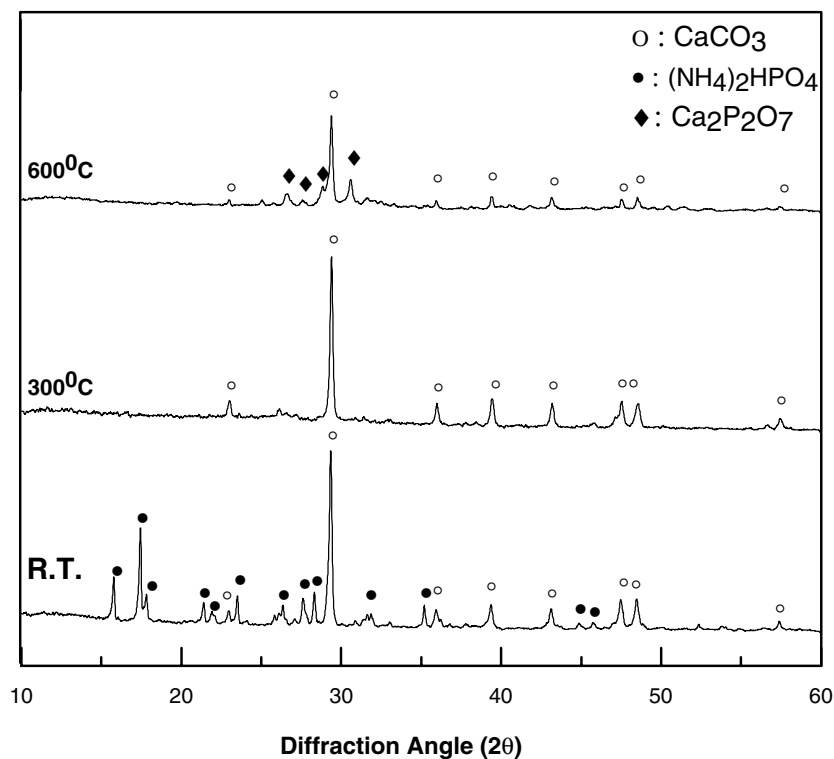


Figure 4 X-ray diffraction patterns of  $\text{CaCO}_3/(\text{NH}_4)_2\text{HPO}_4$  mixture for (a) room temperature (b)  $300^\circ\text{C}$  (c)  $600^\circ\text{C}$ . X-ray diffraction patterns of  $\text{CaCO}_3/(\text{NH}_4)_2\text{HPO}_4$  mixture for (d)  $780^\circ\text{C}$  (e)  $800^\circ\text{C}$ , mark ● indicate the peak of HA, and the other peaks are from  $\beta$ -TCP.

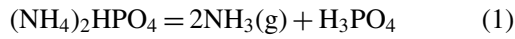
were pre-determined on purpose so that what happened to the powder mixture following the first, second and third peak on the DTG curve (Fig. 1) can be studied. In addition to the phase identification on the patterns in Fig. 4, the XRD results are also listed in Table I.

It is quite obvious that the change after heat-treatment at  $300^\circ\text{C}$  for 3 hours was the decomposition of  $(\text{NH}_4)_2\text{HPO}_4$ . At  $213^\circ\text{C}$  the sudden weight loss (Figs 1 and 2) and the exothermic peak (Fig. 3) are thus attributed to the decomposition. From Fig. 2, the relative weight loss was estimated about 13%, which suggests

TABLE I X-ray diffraction patterns of as-prepared mixture and isothermally heat-treated mixtures of CaCO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Ca/P = 1.5)

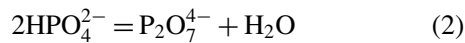
Treatment of the mixture	As-prepared mixture	300°C, 3 hours	600°C, 3 hours	780°C, 3 hours	800°C, 3 hours
Phases	CaCO <sub>3</sub> and (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	CaCO <sub>3</sub>	CaCO <sub>3</sub> and Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	β-TCP and HA	β-TCP

that the decomposition at 213°C is given by

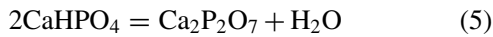
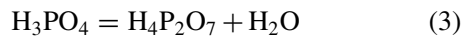


A simple calculation based on above reaction gives the relative weight lose of about 12.1%, the closest to 13% as compared with other possible reactions. The solid product of decomposition was amorphous and was not detected by XRD (Fig. 4).

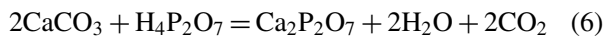
As the temperature was increased, the weight lose became much milder and heat flow was reverse. According to Lin *et al.* [7], HPO<sub>4</sub><sup>2-</sup> starts to be condensed and pyrophosphoric acid was produced until 650°C. The reaction is illustrated by



Reaction (2) is abstract, and the real reactions of this mode are proposed as follows

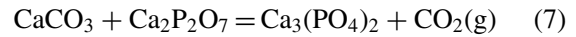


The P<sub>2</sub>O<sub>7</sub><sup>4-</sup> resulting from reaction (3) was also possibly substituted for CO<sub>3</sub><sup>2-</sup> directly to create Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> by additionally consuming CaCO<sub>3</sub>. The reaction is expressed as

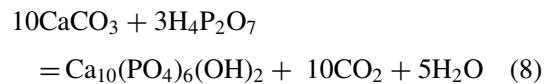


Reaction (4) and (6) involved the decomposition of CaCO<sub>3</sub> which need a relatively large energy supply and high temperature and is usually regarded as a slow and time consuming reaction. Reaction (3) and (5) are so-called condensation of phosphoric roots, which is relatively fast and step by step. In the range of 300°C–600°C, the weight lose curve (Fig. 2) is relatively mild except from 430°C to 505°C. The mild weight loses with almost the same slope below 430°C and above 505°C could be attributed to the slow CaCO<sub>3</sub>decomposition i.e. (4) and (6). But the faster weight lose from 430 to 505°C may be due to the condensation reactions (3) and (5) beside the CaCO<sub>3</sub>decomposition. The decomposition of CaCO<sub>3</sub> released CO<sub>2</sub>, causing the weight lose in the whole range of 300°C–600°C, The evaporating product of the condensation was water, giving an additional fast weight lose in 430°C to 505°C in this stage. In the above argument it is assumed that the condensation (reaction (2)) started at 430°C and terminated at 505°C. XRD showed that the phases in the mixture powder heat treated at 600°C for 3 hours are CaCO<sub>3</sub> and Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (Fig. 4 and Table I), which supports the above argument.

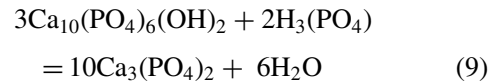
The mild weight lose continued until 755°C. The final fast weight lose occurring at 755–795°C was mainly caused by the transformation of pyrophosphoric roots into orthophosphoric roots with Ca<sup>2+</sup> involved. A very likely reaction is assumed to be



The final phase of the mixture powder after heat treatment at 800°C for 3 hours revealed by XRD (Fig. 4 and Table I) seemingly supports this assumption. However, the XRD on the mixture heat treated at 780°C for 3 hours showed the existence of a small amount of HA (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) in addition to Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (Fig. 4 and Table I), indicating that water was not exhausted until at least 800°C. Accompanying or prior to reaction (7), the following consecutive reactions would rather be predominant.



As temperature was further increased, HA transformed into β-TCP,



Finally up to 800°C, water was completely exhausted and β-TCP was formed. It thus indicates that the fast weight lose at 755–795°C (Figs 1 and 2) was still caused by water evaporation and β-TCP was mainly formed via reaction (8) and (9) instead of reaction (7).

At temperatures above 300°C both water exhausting and CO<sub>2</sub> releasing during the processing of β-TCP formation consumed energy, which was evidenced by the endothermic part of the DTA curve in Fig. 3. Different from DTG and TG, the heat flow for water exhausting and CO<sub>2</sub> releasing can not be individually distinguished and mingle as a wide hill-like peak. The hill was sharply cut at 800°C, suggesting water was exhausted and CO<sub>2</sub> was completely released at this point.

When temperature was enhanced from 800°C up to 1300°C, no more heat flow was detected (Fig. 4), suggesting that the β-TCP prepared in this study was thermally stable until 1300°C. For comparison, commercial β-TCP (Plasma Biotol) was also subjected to the same DTA test and the heat flow curve is shown in Fig. 5. It is quite obvious that at 1150°C an endothermic reaction happened to β-TCP (Plasma Biotol).

β-TCP powder was prepared by heating the powder mixture at 6°C/min up to 1200°C and holding at this temperature for 5 hours. Isothermal heat treatments for 3 hours at different temperatures were conducted on the as-prepared (in this study) and as-received

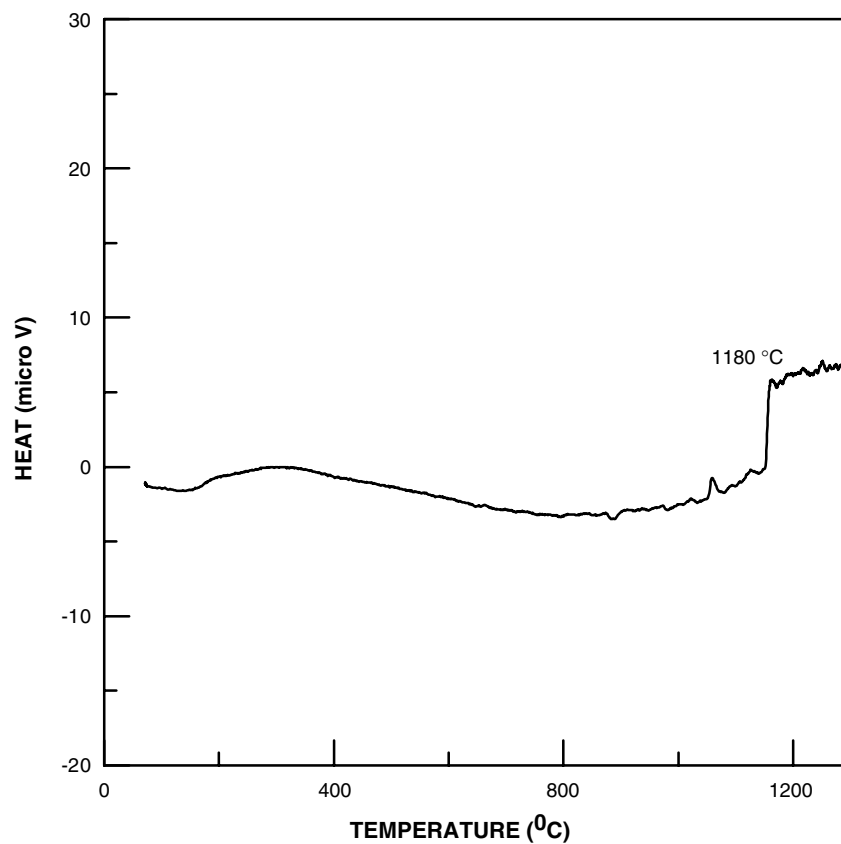


Figure 5 Differential thermal analysis of Plasma Biotal  $\beta$ -TCP powder.

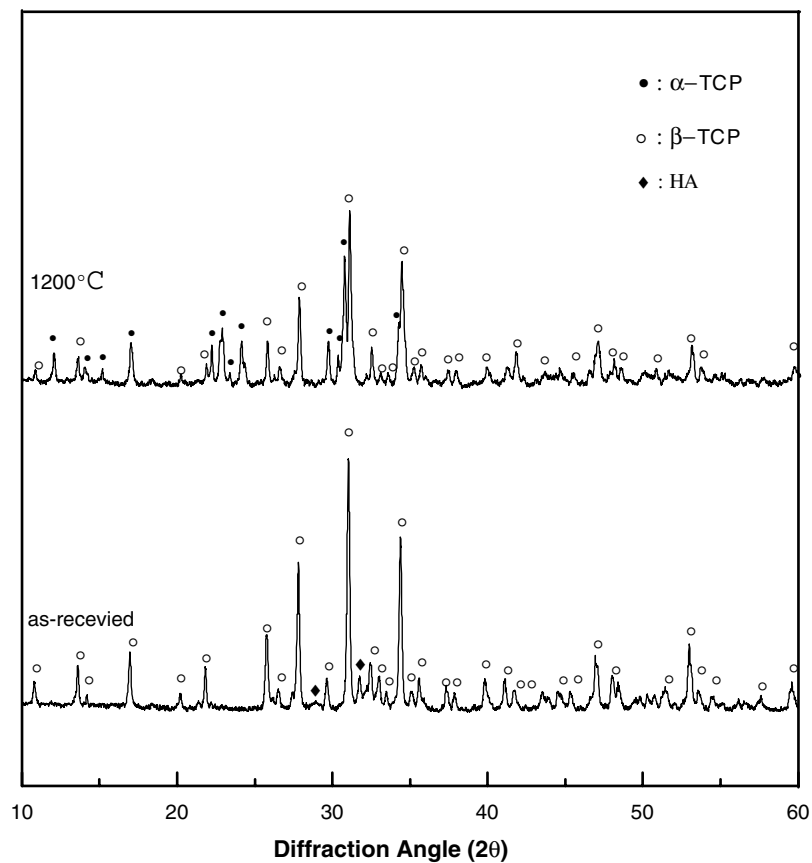


Figure 6 X-ray diffraction patterns of the Plasma Biotal powder for as-received and heated to 1200°C for 5 h.

(Plasma Biotol)  $\beta$ -TCP powders as well. XRD patterns of the as-received and the as-prepared  $\beta$ -TCP powders heat treated at designated temperatures are summarized in Figs 6 and 7, respectively. Fig. 6 shows that as-received Plasma Biotol was single phase of  $\beta$ -TCP, but with  $\alpha$ -TCP formed after 1200°C heat-treated, suggesting that the endothermic shift at 1150°C in Fig. 5 corresponds to the transformation of  $\beta$ -TCP into  $\alpha$ -TCP in the as-received powder. However, in Fig. 7 it is found that the phase transformation of the as-prepared powder in this study did not take place until 1350°C. This is consistent with the fact that the DTA curve in Fig. 3 becomes unpeaked as temperature increased from 800°C up to 1300°C.

On the basis of the XRD data, the lattice parameters of as-prepared and as-received  $\beta$ -TCP powders were calculated by the software attached to the XRD (Rigaku D/max-II B), and summarized in Table II. It is found that *a* and *c* of as-prepared  $\beta$ -TCP in this study are all smaller than the commercial one (Plasma Biotol), and even smaller than the those of standard data.

Ando [8] reported that a tiny amount of magnesium contained in  $\beta$ -TCP enhanced the phase transition temperature of  $\beta$  to  $\alpha$  from 1150°C to 1500°C. Dickens [9] and Schroeder [10] suggested that the enhancement of phase transition temperature were mainly due to the lattice parameter shrinkage cause by the substitution of  $Mg^{2+}$  for  $Ca^{2+}$  in  $\beta$ -TCP. In this study  $CaCO_3$  used did contain 0.6% magnesia, and consequently the

TABLE II Lattice constant of as-prepared, Plasma Biotol, and JCPDs

	<i>a</i>	<i>c</i>
As-prepared	10.411 Å	37.342 Å
Plasma Biotol	10.418 Å	37.395 Å
JCPDs (09-0169)	10.429 Å	37.380 Å

lattice parameters were slightly shortened, which may be the origin of the increase in the temperature at which  $\beta$ -TCP started to transform into  $\alpha$ -TCP.

The prepared  $\beta$ -TCP powder was observed under SEM. Fig. 8 shows typical micrographs of the  $\beta$ -TCP powder as-prepared in this study taken under SEM. The powder is uniaxial and approximately sphere-shaped.

The enhancement of the phase transformation temperature of  $\beta$ -TCP prepared in this study is of significance. In plasma sprayed coatings of  $\beta$ -TCP for metal prostheses used in knee and hip replacement, higher thermal stability of  $\beta$ -TCP leads to a higher performance of the prostheses in human body since the  $\beta$ - $\alpha$  transformation did not take place during coating. Concerning possible incorporation of  $\beta$ -TCP into alumina matrix, the transformation temperature enhancement can also make benefit to the fabrication and final quality of the product, particularly as a fast sintering technology, e.g. spark plasma sintering and microwave sintering, is employed. The fast sintering densifies sample in a very short time so that the reaction between  $\beta$ -TCP and alumina may be

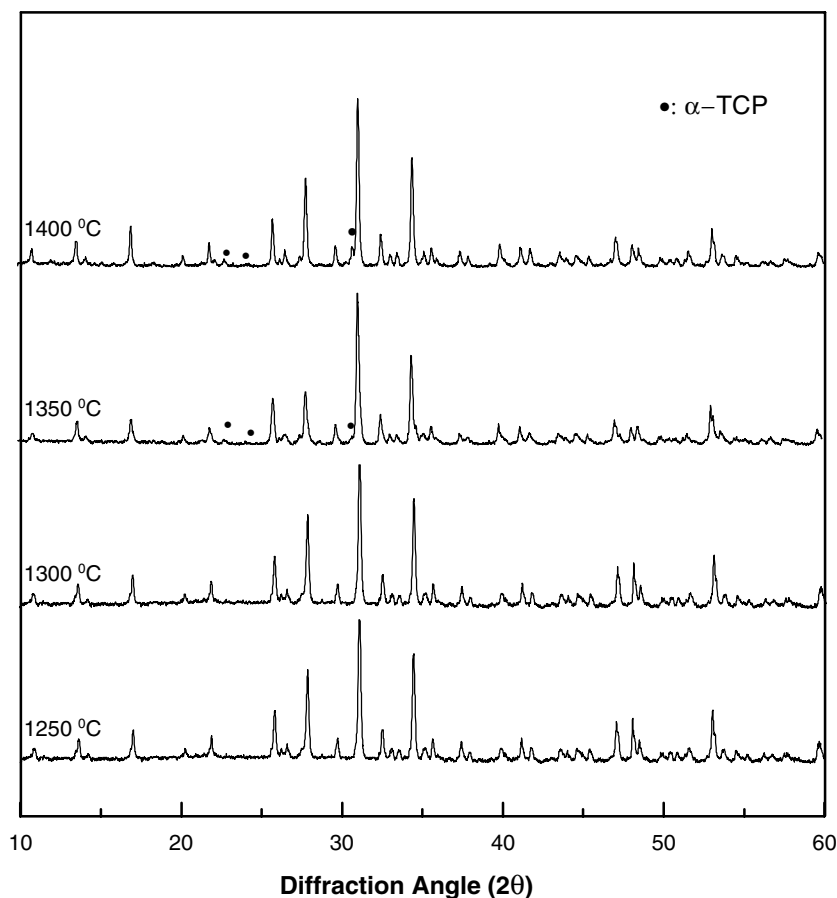


Figure 7 X-ray diffraction patterns of self-prepared  $\beta$ -TCP powder which heated to 1250°C, 1300°C, 1350°C and 1400°C for 5 h. • indicate the peak of  $\alpha$ -TCP and the others are for  $\beta$ -TCP.

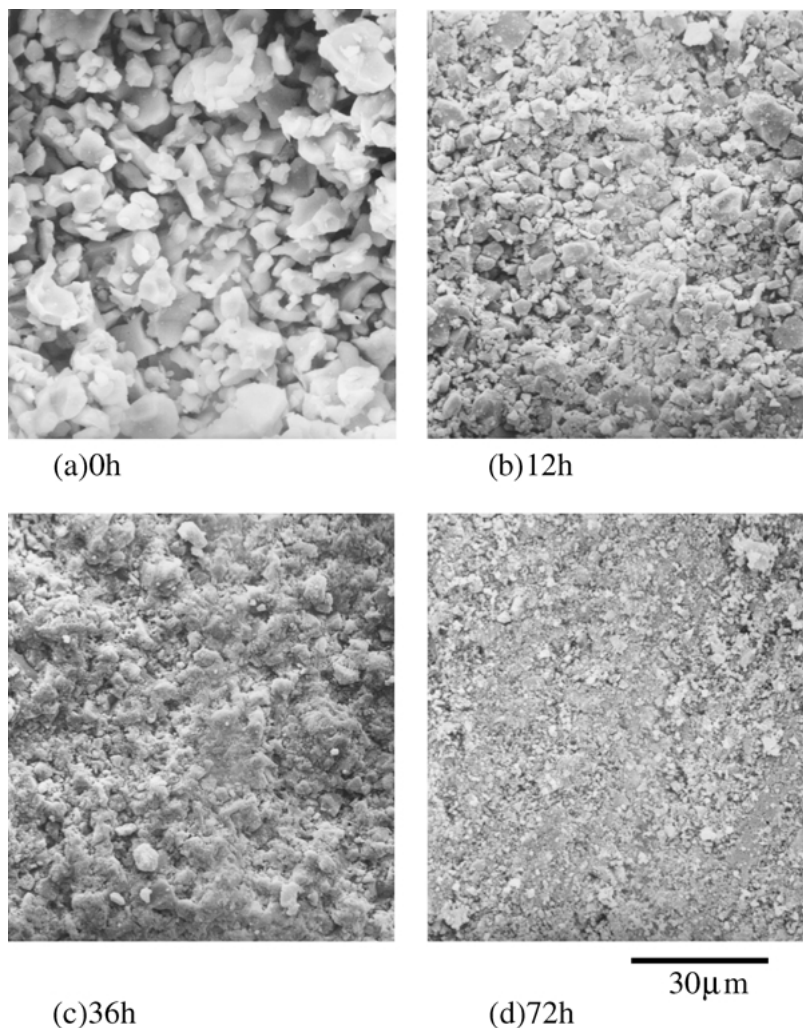


Figure 8 SEM photographs of the  $\beta$ -TCP powder (a) as-prepared and ball milled for (b) 12 h (c) 36 h (d) 72 h. The magnification is 1000 $\times$ .

hindered and the quality in terms of biocompatibility is guaranteed.

#### 4. Conclusions

$\beta$ -TCP powders can be prepared by solid state powder route. The powder has found of high thermal stability, with the phase transformation temperature from  $\beta$  to  $\alpha$  of 1350°C, 200°C higher than commercial  $\beta$ -TCP (Plasma Biotal). The solid reaction process involved weight lose and heat flow, caused subsequently by the decomposition of dibasic ammonium phosphate, water exhaustion during condensation of phosphoric roots and carbon dioxide release.

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