EFFECT OF SINTERING TEMPERATURE ON STRUCTURAL AND MECHANICAL PROPERTIES OF BETA-TRICALCIUM PHOSPHATE

Cho Cho Khin[1], Nay Win Tun[2], Aye Aye Thant[3], and Khin Khin Win[4]

Abstract

β-tricalcium phosphate powders were synthesized by the wet chemical precipitation method starting from calcium nitrate tetrahydrate, $Ca(NO_3)_2.4H_2O$, and diammonium hydrogen phosphate, $(NH_4)_2HPO_4$. The pH of the mixed solution was controlled at pH-10 by adding sodium hydroxide solution. The β-TCP pellets were sintered at 800°C, 900°C, 1000°C, and 1100°C for 6 h each. The structural and mechanical properties of β-TCP pellets were characterized by using XRD, SEM, Hardness tester, and Archimedes' method respectively. The dense microstructure without pores could be obtained at the sintering temperature of 1100°C. The hardness and compressive strength increased with increasing temperature. The maximum compressive strength of β-TCP pellets was obtained at 1100°C. The behavior of bioceramic was investigated such that porosity decreased when the bulk density and temperature increased accordingly. In this research, the sintering temperature at 1100°C provided maximum density and hardness which may be applied as a bone replacement.

Keywords: β-tricalcium phosphate, XRD, SEM, hardness, relative density, porosity

Introduction

Calcium phosphate ceramics are widely used as synthetic bone substitutes. Among the calcium phosphate ceramics, beta-tricalcium phosphate bioceramics are widely used for hard tissue regeneration due to their excellent biocompatibility and their close similarity to biological apatite present in human bones. β-TCP is known to be highly resorbable in vivo with new bone ingrowths replacing the implanted β-TCP [Yong-Seok, J., et al., 2018]. In the physiological environment, they can gradually degrade, absorb, and promote bone growth. Ultimately, they are capable of replacing the damaged bone with new tissue [Behzad, M., et al., 2012]. It has good biodegradability and a higher dissolution rate in the body's environment after implantation, which is absorbed and replaced by new bone. In the present research, the wet chemical precipitation method was carried out to prepare β-TCP and the effect of sintering temperature on structural and mechanical properties of β-TCP pellets were investigated.

Materials and Method

Experimental Procedure

β-TCP powders were synthesized by the wet chemical precipitation method starting from calcium nitrate tetrahydrate with diammonium hydrogen phosphate. The Ca:P molar ratio of β-TCP is 1.5. Keeping that ratio constant, the amounts of required raw materials were calculated. Calcium nitrate tetrahydrate and diammonium hydrogen phosphate solutions were prepared by dissolving the crystals in distilled water and stirred at room temperature. The prepared solution of $(NH_4)_2HPO_4$ was added slowly drop-wise into the $Ca(NO_3)_2.4H_2O$ solution. The pH of the mixed solution was controlled at a pH value of 10 by adding sodium hydroxide solution. The obtained white suspension was stirred for 12 h. The synthesized precipitate was washed with distilled water as well as ethanol. After filtration, the filter cake dried at 80°C for 24 h. The dried powders were calcined at 700°C for 2 h. The synthesized β-TCP powders were pressed into pellets by the

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hydraulic press. The pellets were sintered at 800°C, 900°C, 1000°C, and 1100°C for 6 h each. The phase formations of these samples were characterized by using X-ray Diffraction analysis. The morphological features of β-TCP pellets were studied by a scanning electron microscope. The values of hardness were measured by using the hardness tester (EH-01). The compressive strengths were calculated from the hardness data. The bulk density and porosity were measured by using Archimedes' method. Figure 1 shows the flowchart of the sample preparation processes of β-TCP sample for pH-10.

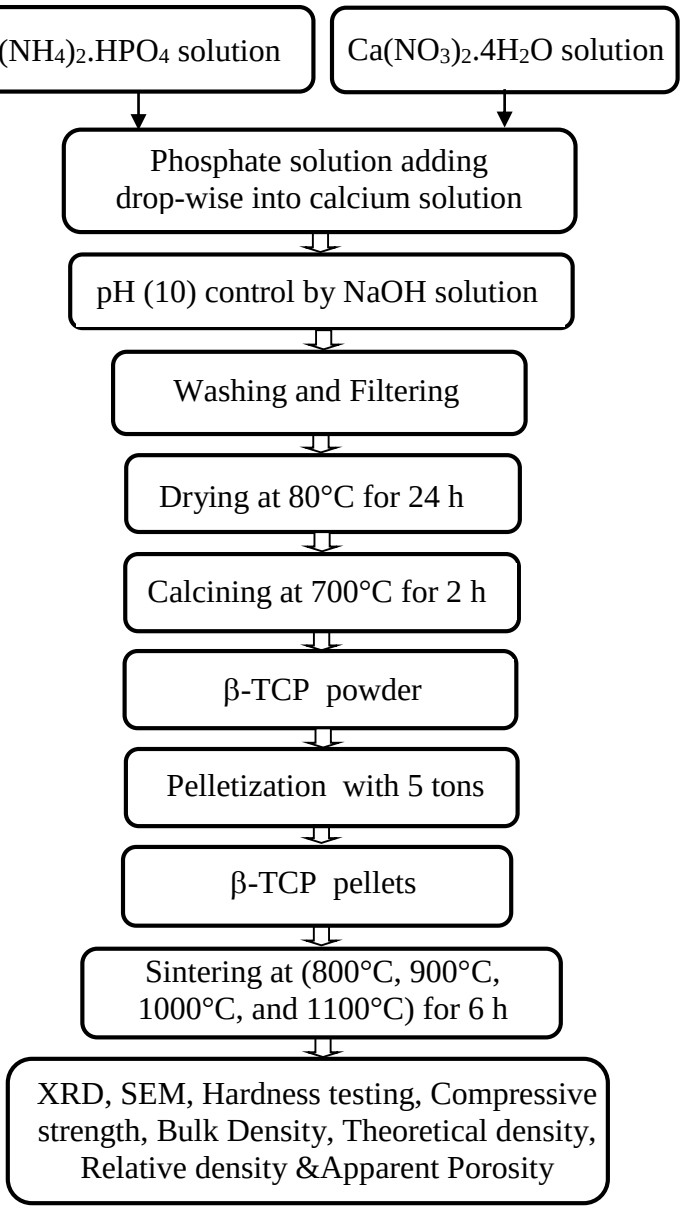

Figure 1 Flowchart of sample preparation processes of β-TCP sample for pH-10

Results and Discussion

Phase Formation by XRD Analysis

X-ray Diffraction (XRD) analysis was carried out to study the phase formations of β-TCP pellets. The XRD spectra of β-TCP pellets at 800°C, 900°C, 1000°C, and 1100°C for pH-10 is shown in Figure 2.

All peaks were well matched with the standard profile of whitlockite $Ca_3(PO_4)_2$. The XRD spectra exhibit that the phase in each sintered pellet is the rhombohedral structure of β-TCP. Thus, the β-TCP pellet was indicated the pure phase. The peaks were sharper as the sintering temperature was increased. The results show that the sintered pellets contain only a single phase β-TCP structure.

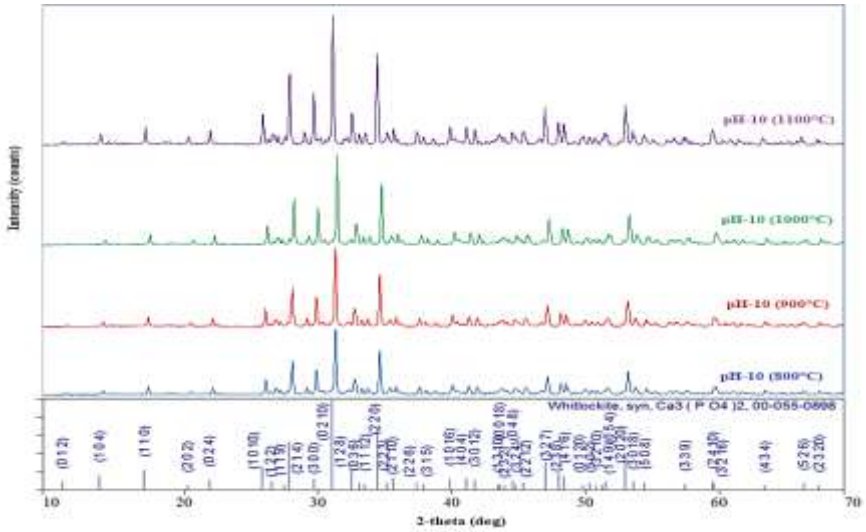

Figure 2 XRD spectra of β-TCP pellets sintered at 800°C, 900°C, 1000°C, and 1100°C for pH-10

Determination of Lattice Parameters, Crystallite Size, and Theoretical density

The lattice parameters 'a' and 'c' were calculated by using the 'd' value of the intense peak. The crystallite sizes were calculated by Debye Scherrer equation using FWHM and Bragg angle obtained from the XRD data. The values of crystallite size and lattice parameters of sintered pellets at 800°C, 900°C, 1000°C, 1100°C for 6 h are summarized in Table 1. It was investigated that the lattice parameters of the pellets well agree with the typical values for β-TCP structure as discussed in other research of β-TCP [Yashima, M., et al., 2003]. It was found that the crystallite size is in the nano-range and increased with increasing temperatures in Figure 3.

According to the XRD data, the unit cell volume in the β-TCP pellets was calculated and then the theoretical densities of the β-TCP pellets were calculated. The results were represented in Table 1. It was found that the theoretical densities of the β-TCP pellets lie in the range of 3.02 g cm^{-3}- 3.07 g cm^{-3}. However, the literature value of the theoretical density for β-TCP pellet is 3.07 g cm^{-3}. Thus, the obtained theoretical density of pure β-TCP pellet is in agreement with the literature value.

Table 1 The value of crystallite size, lattice parameter and theoretical density of β-TCP pellets for pH-10

Sintered Temperature (°C)	Crystallite Size D (nm)	Lattice Parameter		Theoretical density (g cm^{-3})
		'a' (Å)	'c' (Å)	
800	58.15	10.44	37.38	3.07
900	62.52	10.46	37.44	3.05
1000	69.21	10.48	37.60	3.02
1100	71.83	10.44	37.40	3.06

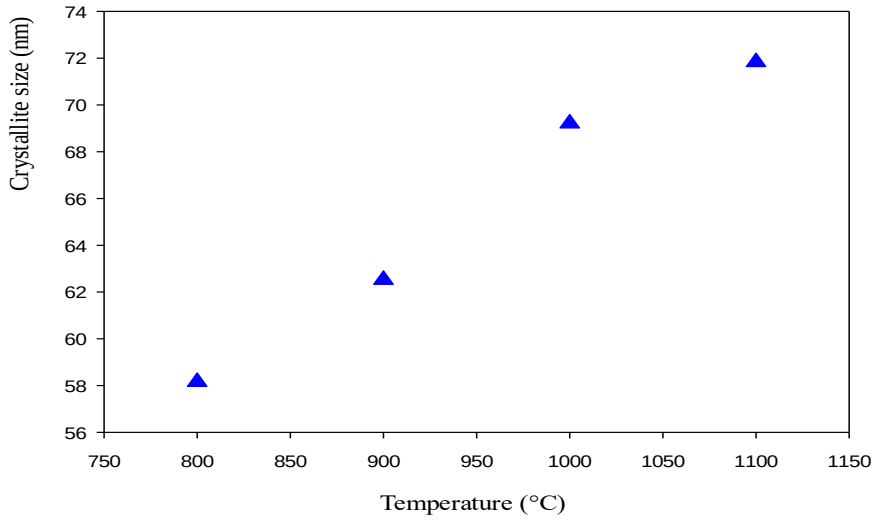

Figure 3 The crystallite size of β-TCP pellets at different sintering temperature for pH-10

Morphological Feature by SEM Analysis

The surface morphology features of β-TCP pellets were studied by a scanning electron microscope. SEM micrographs of β-TCP pellets obtained by sintering at 800°C, 900°C, 1000°C, and 1100°C for 6 h are shown in Figure 4 to Figure 7 respectively. The sintering temperature at 800°C in Figure 4 shows the particles in the sample were irregular in shape and highly agglomerated microstructure. The sintering temperature at 900°C in Figure 5 shows the highly reactive irregular particles in the sample were joined by neck growth and a continuous pore channel was formed. The fracture surface of the sample sintered at 1000°C in Figure 6, the grain boundaries and isolated pores were visible. Sintering temperature at 1100°C in Figure 7, the surface of the sample was highly dense and larger grain size with no pores. From the SEM micrographs of pellets that were sintered at different temperatures, it is noted that the grain size is increased with increasing temperatures as shown in Table 2. Therefore, it can be said that the pores become smaller with the increase in sintering temperature, and finally the dense microstructure without pores could be obtained at the sintering temperature of 1100°C.

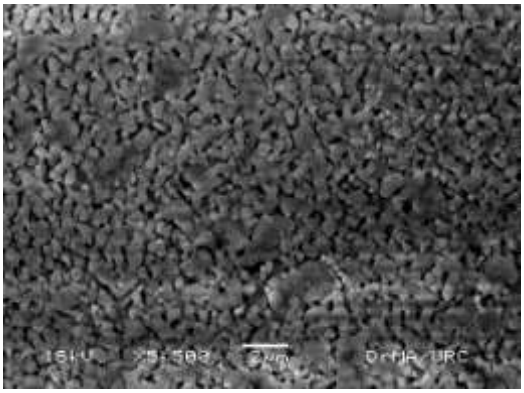

Figure 4 SEM micrograph of β-TCP pellet at 800°C for pH-10

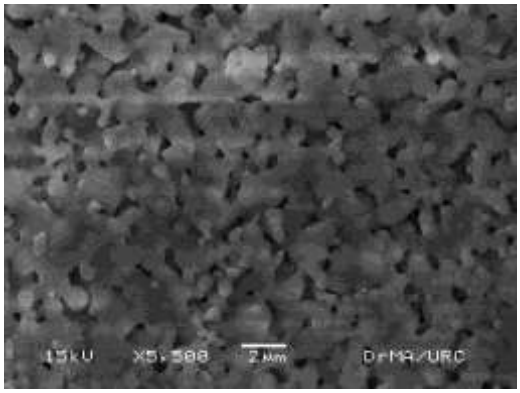

Figure 5 SEM micrograph of β-TCP pellet at 900°C for pH-10

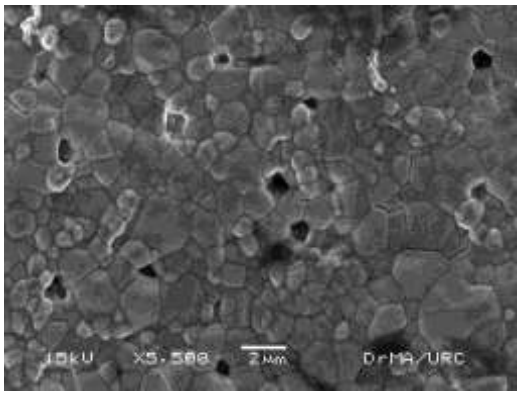

Figure 6 SEM micrograph of β-TCP pellet at 1000°C for pH-10

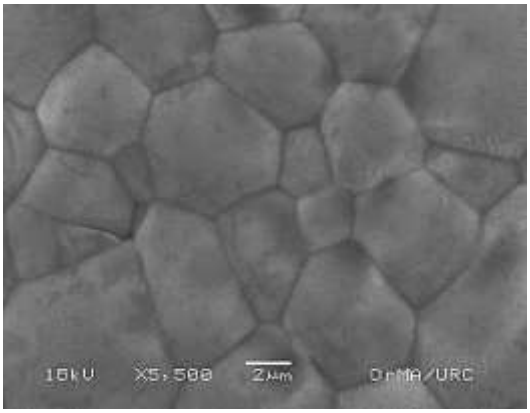

Figure 7 SEM micrograph of β-TCP pellet at 1100°C for pH-10

Table 2 The average value of grain size of β-TCP pellets at different sintering temperatures for pH-10

Sintered Temperature (°C)	Grain size (μm)
800	0.82
900	1.01
1000	1.06
1100	4.38

Study on Mechanical Properties of Sintered β-TCP Pellets

In this study, the thickness and diameter of the β-TCP pellets for pH-10 were measured by using a digital caliper. And then the values of the hardness of the β-TCP pellets were measured by using the hardness tester (EH-01). The compressive strengths of the β-TCP pellets were calculated by using the Hertz equation. The effect of sintering temperature on the hardness and compressive strength of β-TCP were investigated and the data are summarized in Table 3. The variation of hardness and compressive strength of β-TCP pellets with different temperatures are shown in Figure 8 and Figure 9 respectively. It was found that the hardness increases with increasing sintering temperature. The maximum hardness is found to be 484.8 N at 1100°C. The compressive strength of the sample which is determined from the hardness value shows the same trend as the hardness accordingly. The maximum compressive strength was found to be 10.29 MPa at 1100°C. It can be said that the hardness and compressive strength of β-TCP is increased with increasing sintering temperature.

Table 3 The values of hardness and compressive strength of β-TCP pellets for pH-10

Sintered Temperature (°C)	Hardness P (N)	Compressive Strength σ_{comp} (MPa)
800	139.8	2.86
900	172.3	3.56
1000	263.3	5.52
1100	484.8	10.29

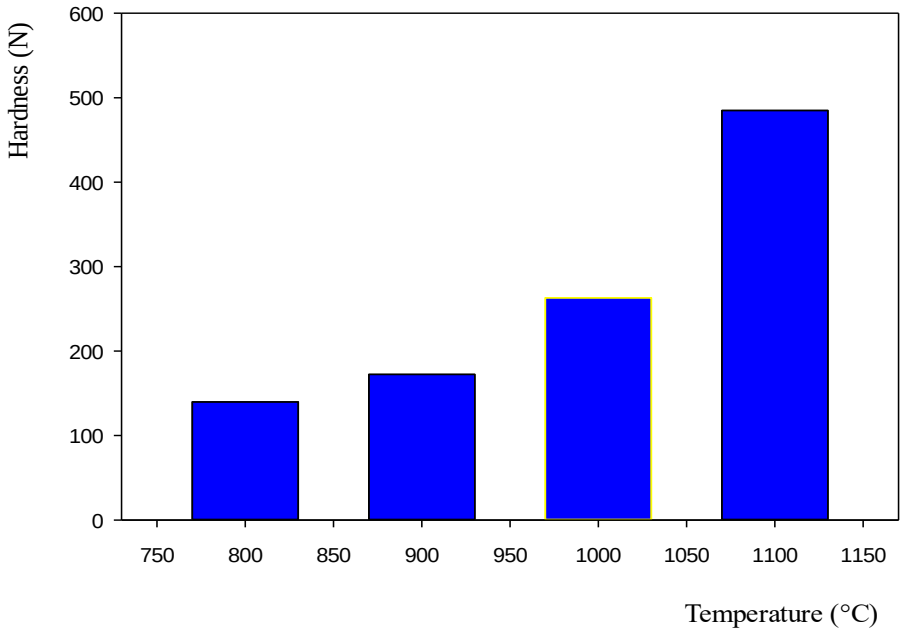

Figure 8 The variation of hardness value of β-TCP pellets at different sintering temperature for pH-10

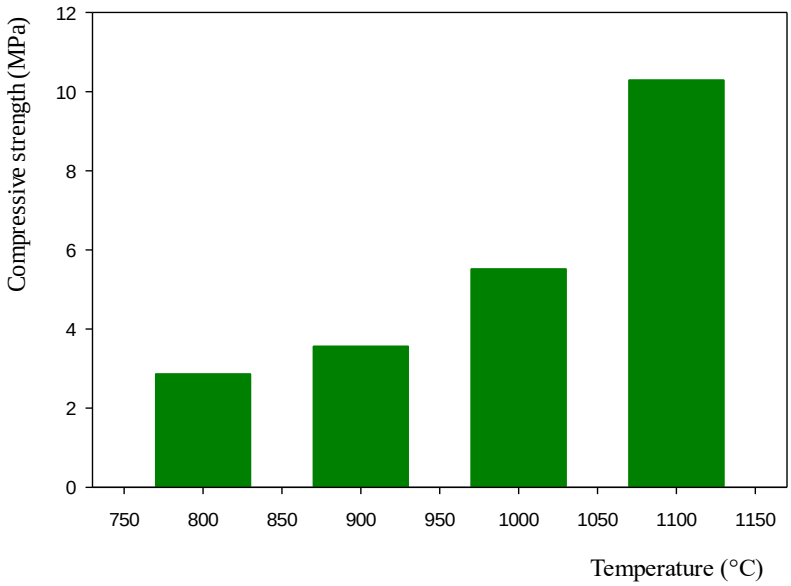

Figure 9 The variation of compressive strength of β-TCP pellets at different sintering temperature for pH-10

Estimation of Bulk Density, Relative Density, and Apparent Porosity of β-TCP Pellets

The bulk density and apparent porosity of the β-TCP pellets sintered at different temperatures for pH-10 were measured based on the Archimedes' method. The measured bulk density and apparent porosity of β-TCP pellets were represented in Table 4. The bulk density increases with increasing temperature and the porosity decrease with increasing temperature accordingly. It was found that the sample β-TCP at 1100°C exhibits the largest bulk density with the smallest porosity in Figure 10.

Figure 11 shows the relative densities of the β-TCP pellets sintered at different sintering temperatures for pH-10. It was found that relative density is increased with increasing sintering temperature. The relative density of β-TCP pellets increased up to 93.81% at 1100 °C. It can be said that the β-TCP pellet sintered at 1100°C was composed of a highly compact structure.

Table 4 The values of bulk density, relative density, and apparent porosity of β-TCP pellets for pH-10

Sintered Temperature (°C)	Bulk density (g cm^{-3})	Relative density (%)	Apparent Porosity (%)
800	2.65	86.32	26.47
900	2.71	88.27	23.53
1000	2.76	89.90	18.18
1100	2.88	93.81	9.37

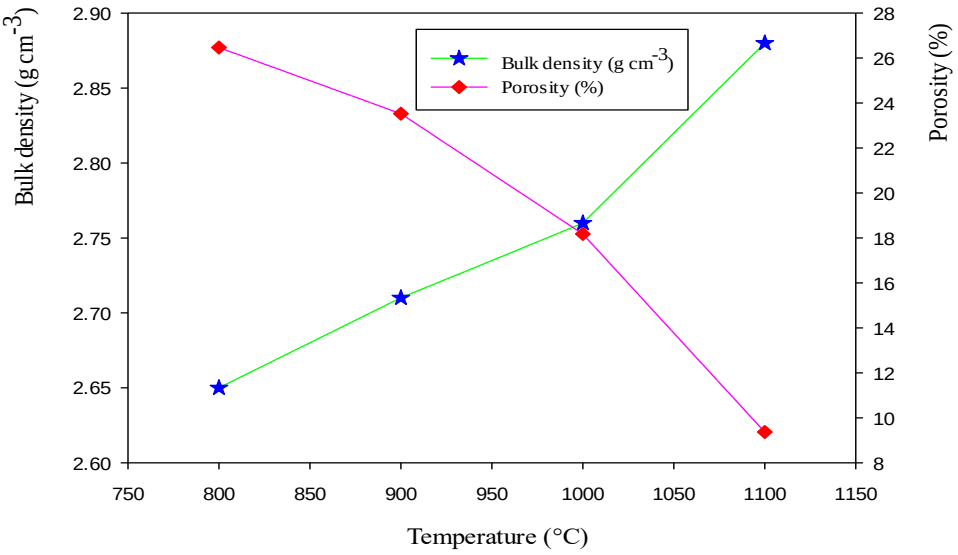

Figure 10 Comparison between bulk density and porosity of β-TCP pellets at different sintering temperature for pH-10

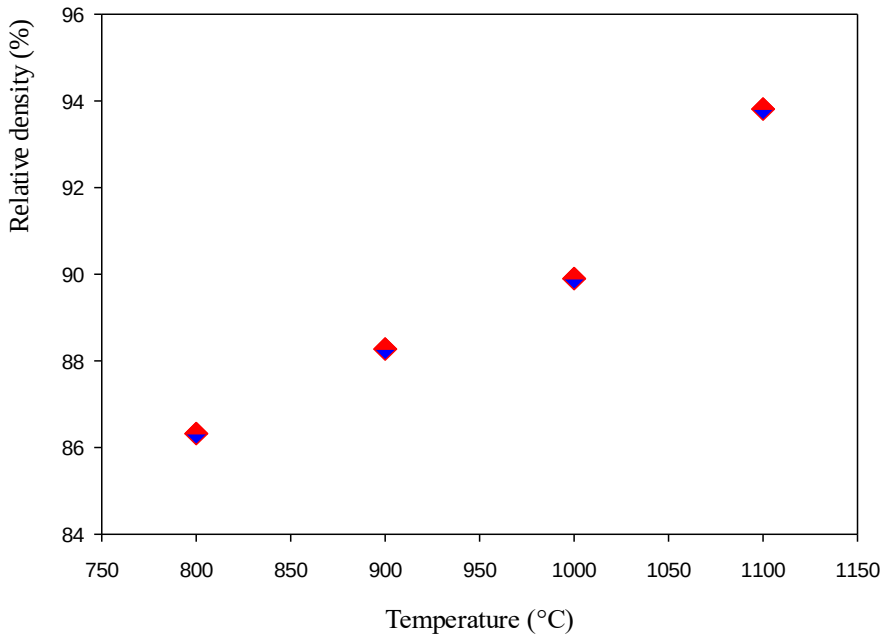

Figure 11 The relative density of β-TCP pellets at different sintering temperature for pH-10

Conclusion

β-TCP pellets were synthesized by the wet chemical precipitation method. The XRD analysis has revealed that the phase precipitated out in the samples is the rhombohedral structure of β-TCP. The lattice parameters and theoretical density of β-TCP pellets well agree with the typical values for β-TCP structure. Moreover, the crystallite size of β-TCP is obtained in nano-range and found to be increased with increasing temperatures. The XRD results proved that the single phase β-TCP was successfully obtained at different sintering temperatures with increased crystallite size. After sintering at different temperatures, the average grain size has increased with

increasing temperature. This increase in grain size with the temperature well agrees with the increase in crystallite size. This finding pointed out that the synthesis route is consistent with different sintering temperatures. The hardness and compressive strength of β-TCP pellets are found to increase with increasing sintering temperature. The hardness and compressive strength of β-TCP exhibit a larger value at 1100°C. The bulk density and relative density increase with increasing temperature and the porosity decreases with increasing temperature accordingly. It was found that the sintered β-TCP sample at 1100°C possesses the lowest porosity as it exhibits the largest compressive strength and bulk density with no pores in SEM analysis. The results showed that an increase in sintering temperature decreased the porosity and increased the mechanical properties of β-TCP. The results proved that the sintering temperature at 1100°C showed the most optimum properties of hardness, relative density, and microstructural features. Based on the results obtained, it is concluded that the sintering temperature could effect on structural and mechanical properties of beta-tricalcium phosphate.

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