CHAPTER 4

Discussions

The aim of the experimental plan was to study mechanism of sintering for synthesis HA using calcium carbonate ($CaCO_3$) and ammonium dihydrogen phosphate ($NH_2H_2PO_4$) powders. This mechanism was used two types of powders for mixed and ground and forming as desired shape, then used to high temperature from external. This temperature has effect on reaction together with two particles for synthesis of single phase HA.

This thesis was not studied of Ca/P mole ratio 1.70 and up because phase diagram of CaO and P_2O_5 showed the stoichiometric ratio of calcium and phosphorus of HA was 1.67, and this research had objective for synthesis HA from this ratio by studied from mole ratio which closed and variable with ratio of 1.65, 1.66, 1.68 and 1.69 for avoided the formation of impurity phases. According to phase diagram various types had seven phases showed in this table [57].

Ca/P	Mineral name	Formula	Chemical name
1.0	Monetite	$CaHPO_4$	Dicalcium phosphate (DCP)
1.0	Brushite	$CaHPO_4.2H_2O$	Dicalcium phosphate Dihydrate (DCPD)
1.33	-	$Ca_8(HPO_4)_2(PO_4)_4.5H_2O$	Octacalcium phosphate (OCP)
1.43	Whitlockite	$Ca_{10}(HPO_4)(PO_4)_6$	-
1.50	-	$Ca_3(PO_4)_2$	Tricalcium phosphate (TCP)
1.67	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	-
2.0		$Ca_4P_2O_9$	Tetracalcium phosphate

For mole ratio of Ca/P range from 1.5 to 1.67 had formula of calcium deficient HA (CDHA). This ratio had value less than the stoichiometric value of 1.67, and could be prepared by solid state reaction of this research. The direction of phase formation when compared with phase diagram CaO and P_2O_5 [57] found that with Ca/P mole ratio of 1.65 to 1.69 at 1200, 1250 and 1300 °C had HA, TCP and CaO phases because $CaCO_3$ decomposed into CaO and released CO_2 gas and sintered below 1360 °C.

The parameter which provided to considered influence of Ca/P mole ratio, an isothermal sintering and soaking time on phase formation. From this condition, influence of Ca/P mole ratio had higher than isothermal sintering temperature and soaking time and could be explained by driving force for sintering. The driving force for sintering must be consisted the total free energy (ΔG_T) of the system:

$$\Delta G_T = \Delta G_v + \Delta G_{gb} + \Delta Gs$$

where ΔG_v, ΔG_{gb} and ΔG_s represent the change in free energy associated with the volume, boundaries and surfaces of the grains, respectively. The rate of diffusion depends on the type and concentration of anions and cations in ionic-covalent ceramic and volume diffusion, grain boundary diffusion and surface diffusion, so an understanding of the diffusing of ions structure and the change in point defect had important than the temperature and soaking time [56].

The reaction rate from the results of DTA/TG at temperature range from 1100 to 1300 °C for 2 to 5 hours were formed carbonates HA type B, where the CO_3 groups were substituted by the PO_4 groups. The carbonate incorporation might be the carbonation of $CaCO_3$ or during the reaction at temperature range 775 to 867 °C

$$\beta\text{-}Ca_2P_2O_{7(s)} + 2CaCO_{3(s)} + CaO_{(s)} \xrightarrow{\sim 775 - 867^{\circ}C} Ca_3(PO_4)_{2(s)} + Ca_{10-x}(V)_x(PO_4)_{6-x}(CO_3)_x$$
$$+ Ca_{10-x}(V)_x(PO_4)_{6-x}(CO_3)_x(OH)_{2-2x}V_{x(s)} \qquad (OH)_{2-2x}V_{x(s)} + CaO_{(s)} + CO_{2(g)}$$

where; V = vacancies from OH^{-} atoms or point defects of Ca^{2+}, PO_4^{3-}. At higher temperature range from 867 to 1100 °C and from 1100 to 1300 °C, respectively.

$$Ca_3(PO_4)_{2(s)} + Ca_{10-x}(V)_x(PO_4)_{6-x}\,(CO_3)_x\,(OH)_{2-2x}V_{x(s)} + CaO_{(s)} \xrightarrow{\sim 867\text{ - }1100^{\circ}C}$$

$$Ca_3(PO_4)_{2(s)} + CaO_{(s)} + Ca_{10-x}(V)_x(PO_4)_{6-x}\,(CO_3)_x\,(OH)_{2-2x}O_xV_{x(s)}$$

$$Ca_3(PO_4)_{2(s)} + CaO_{(s)} + Ca_{10-x}(V)_x(PO_4)_{6-x}\,(CO_3)_x\,(OH)_{2-2x}O_xV_{x(s)} \xrightarrow{\sim 1100\text{ - }1300^{\circ}C}$$

$$Ca_3(PO_4)_{2(s)} + CaO_{(s)} + Ca_9(V)(PO_4)_5\,(CO_3)O(V)_{(s)}\text{ ; if, } x = 1$$

$$Ca_3(PO_4)_{2(s)} + CaO_{(s)} + Ca_9(V)(PO_4)_5\,(CO_3)O(V)_{(s)} \xrightarrow{\text{annealing at }850^{\circ}C\text{ for 1 h and cool down}}$$

$$Ca_3(PO_4)_{2(s)} + CaO_{(s)} + Ca_9(PO_4)_6\,(CO_3)O(OH_2)_{(s)}\text{ (rehydration to restore the water)}$$

During the cooling stage from firing profile, an annealing stage at 850 °C for 1 hour, and then cool down to room temperature. This assumed that this temperature range presented partial rehydration process. The rehydration process was started the diffusion and mobility of OH^{-} and H^{+} groups. These ions might diffuse to surface of materials or partial of structure which not complete of reaction. Some researcher found that oxyapatite phase was stable and would not undergo any reverse phase transformation. In this study, after high temperature until to room temperature, oxyapatite would be rehydrated OH^{-} ions form as HA, which this results confirmed by FTIR analysis.

This result showed that the intensity peak of OH^{-} stretching band and free OH^{-} ions of samples had lower transmittance than of theoretical HA. This result could be explained by [83] who indicated the trivalent anionic phosphate sites (PO_4^{3-}) might be occupied by both the bivalent ions hydrogen phosphate and carbonate while the monovalent anionic site substitution of hydroxyl (OH^{-}) was possible only by CO_3^{2-}. The phosphate site could not accepted vacancies, probably because the trivalent anions were quite large and vacancies would no stabilized the lattice and calcium sites could also be occupied by other cations and could also accepted vacancies up to a maximum of two sites out of the 10 existing in stoichiometric apatites [83].

CO_3^{2-} could substitute for PO_4^{3-} (B substitution) or for OH^{-} (A substitution). A and B carbonated apatite could be distinguished on the basis of their different lattice constants, and by the different positions of the CO_3^{2-} infrared absorption bands. In biological apatite, CO_3^{2-} substituted mainly for PO_4^{3-} in B-tpye apatite [84].

This research created porosity and decreased significantly bulk and apparent density and strength. If the porosity became larger, then strength would be affected significantly, when it would reached a size larger than the preexisting defect which might be related to powder processing, compaction and isothermal sintering. A tendency of strength loss at higher temperature depends on grain growth and caused by abnormal grain growth at higher isothermal sintering. This research might be unprocessed powder before compact powder and heating, which affected on non-uniform grain structure of powder.

According to SEM result, a wide distribution in particle size of the starting powder was trend to support not uniform grain structure at 1300 °C. Result of SEM was starting grain size created forces on the grain boundaries that caused abnormal grain growth. It was inferred that a grain larger than twice the average size in two dimensions and would be outside the maximum sustainable size and would growth abnormally. Surprisingly, when the evolution of large grains in a fine grained matrix was analyzed theoretically, it was found that large grains not undergo abnormal or runaway grain growth. Grains larger than twice the critical size might develop abnormal due to the large driving force from highly curved boundary between the large grain and the matrix [85].

From this research, it could be seen that thermal decomposition reaction bring about a changed in the HA/β-TCP/CaO phases content of material, they had effect on the resorption rate in vivo. In addition, the presence of CaO and possible transform to $Ca(OH)_2$ caused by absorbed moisture could lead to internal stress and cracking in the material body due to volume change. Therefore, samples need to be avoided moisture from atmosphere by keep in desiccators.

One hypothesis was intimate contact between the HA and β-TCP grains achieved during sintering leads to high stress at grain boundary. This research might be occurred partly arising from the thermal expansion coefficient mismatch between HA and β-TCP, particular along the c-axis of crystals.

Another important goal of this research was studied in laboratory animal for determined the biocompatibility of the implanted material. This research selected the optimize condition which were mole ratios of 1.69 and 1.65 at 1300 °C for 2 hours. The changes of time periods could be provided a continuous of inflammatory stimulus. The inflammation was compared with the samples ratio of 1.69 and 1.65 for HA phase content of 91.44 % and 69.13 %, respectively. This experiment revealed that overall throughout of time periods from 3 days to 180 days. This result was indicated that stability of sample depends on quantity of HA. For instance, the solubility rate of sintered HA in subcutaneous tissue was 0.1 mg/year [86], and β-TCP was biodegradable and when implanted in tissue β-TCP could be dissolved 12.3 times in acidic medium and 22.3 times in basic medium than HA [87]. An apparent porosity was factor of support infiltration of cells into the samples more than 50 % of every periods of implantation. This hypothesis had been observed from apparent porosity was 51.2 % with ratio of 1.65, but with ratio of 1.69 was 24.37 % and SEM analysis of samples with ratio of 1.69 found that pore size was range from 1 to 10 μm which cells could not be infiltrated into the ceramic body because cells could be good infiltrated into the ceramic body size of 100 to 500 μm [25]. This phenomenon might not been supported osteoconduction properties of biomaterial. The calcification was another factor of obstruction cells that infiltrated into the ceramic body due to remained of CaO phase into microstructure of samples. Calcium ions could leak into body tissues and prevent muscle relaxation. On one hand, CaO might be increased stiffness of ceramic body.