CHAPTER II

MATERIAL PREPARATION AND CHARACTERIZATION

In chapter 1, it was pointed out that hydroxyapatite was studied for dental and clinical applications since it was the natural mineral phase of bone and teeth and had proven to be biologically compatible with these tissues. In this study, the hydroxyapatite powders were obtained from cattle bones according to the method of Sombuthawee. The process of fabrication was normal sintering using different temperatures and times to study their effects on microstructure, bulk density, and apparent porosity of cattle bone material. Main experimental equipments used for the study in this chapter are shown in Figs. A. 1 to A. 5.

2.1 Materials and Methods

2.1.1 Calcination

Bone samples from the middle part of cow legs as shown in Fig. 2.1 and calcined by preheating to the temperature 700° C within 4 hours and kept at that temperature for 3 hours to extrude organic substances such as fat from bone. After calcination the product was wet ground into a fine powder using a ball mill method. The particle suspended in the slurry was screened through a 140 meshscreen and was dried at 110° C.

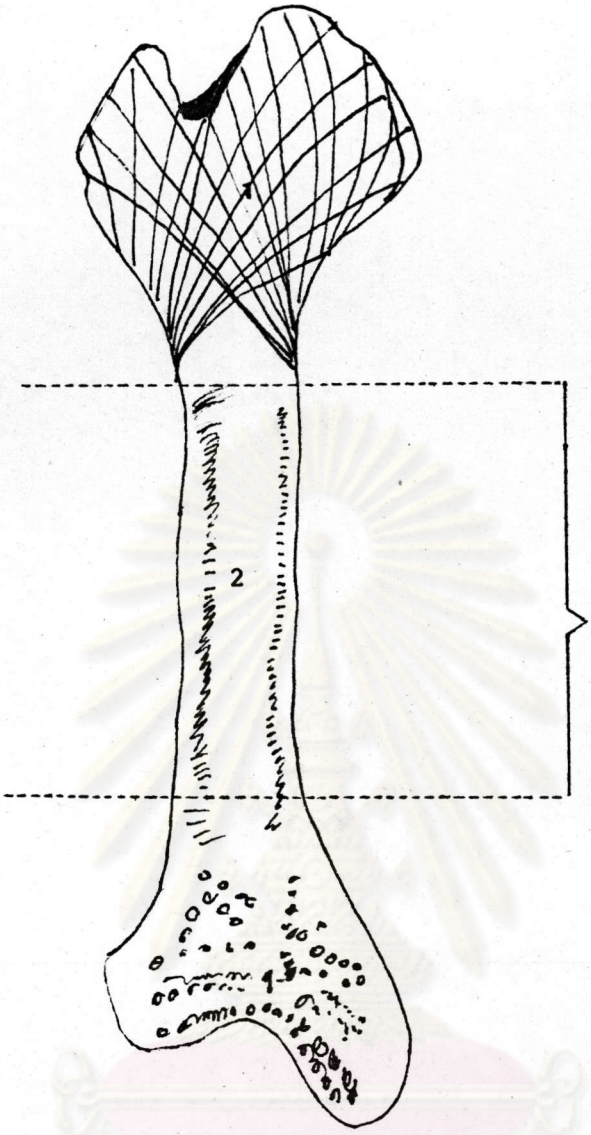

Fig. 2.1 Macrostructure of a bone.*

1 - spongy bone

2 - compact bone

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*According to Sombuthawee's work (5), phases of buffalo bones and cow bones at elevated temperatures are the same.

2.1.2 Pressing

Pressing was accomplished for forming the powders into the required shape. An organic material was neccessary for use with these powders to assure that the compact powder were not quite apt to be broken in handling. The selected binders which were PVA, glycerine, and water were mixed together with the suitable ratio. The powder premixed with the binders were then placed into the rectangular cavities of iron die of dimension 7.5 cm x 7.5 cm x 1.0 cm and pressure were applied to 17.89 MPa (2,596 psi) by the hydraulic press.

2.1.3 Sintering

Sintering took place after putting the compacts of cattle bone powders in the electric furnace Heraeus K 1700/1 and firing in air (to the sintering temperature) with 50° C/min. The samples were allowed to room temperature after firing.

Sintering was carried out at 1100 to 1360° C for 0.5 hr. Change in microstructure, bulk density, and porosity were observed after heating. The three groups of samples fired at 1200, 1250, and 1345° C for 0.5, 1, and 3 hrs were prepared to observe the effect of time.

2.1.4 Characterization of the ceramic

a) X-ray diffraction

Fired samples were crushed to find powder and examined by X-ray diffractometer with copper K α radiation and Ni filter using time constant 2 s and a scan rate of 1° min^{-1}.

The peaks were recorded with a chart drive speed of 1 cmmin^{-1} and the diffraction angle 2 θ was varied from 10° to 60°.

b) Scanning electron microscopy

Fresh fractures of calcined bone and fired samples were prepared to examine microstructure. After coating the fracture surfaces with a thin layer of gold, the pieces were direct observed by scanning electron microscope. Grain size and pore fraction were observed from the micrographs.

c) Physical property measurements

The samples fired at each temperature for a constant duration time and ones fired for various duration times at a canstant temperature were measured density and porosity to see how temperature and time influence these properties. According to the technique defined in American Society for Testing and Material Specification ASTM C373 (13) five pieces with freshly fracture surfaces of dried samples were represented for each physical testing.

2.2 Result

2.2.1 Calcined material

The white particle of ceramic powder was affirmed by X-ray diffraction showing the peaks of the hydroxyapatite structure since there was a good agreement between the sample and the JCPDS data for hydroxyapatite (Fig. 2.2). The micrograph of agglomerated powder in filtered cake was shown in Fig. 2.3.

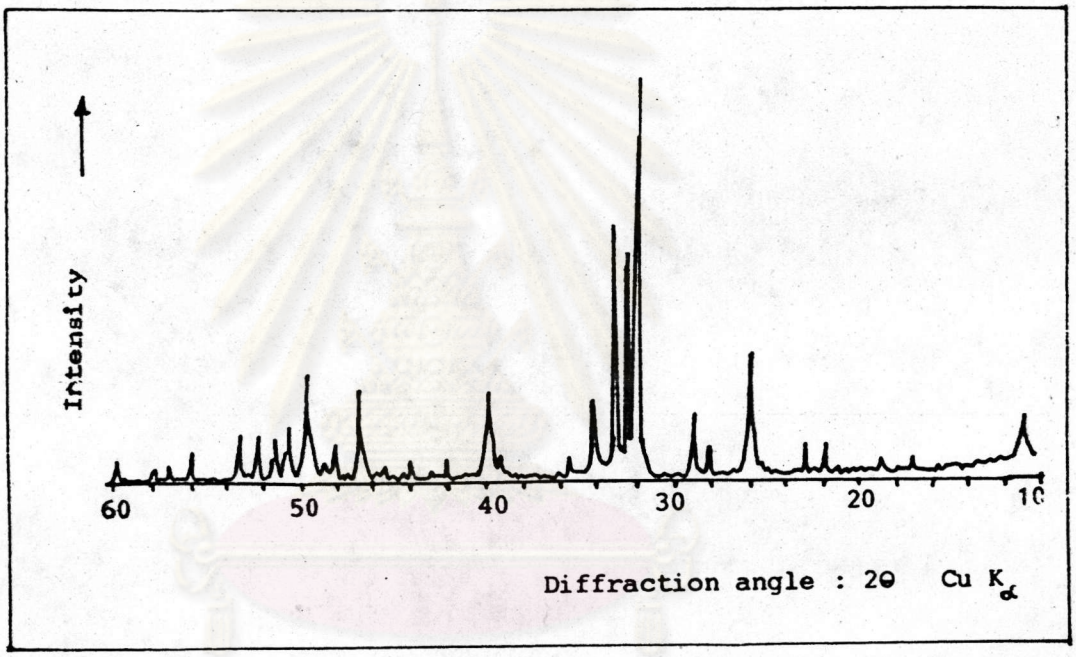

Fig. 2.2 X-ray diffraction peaks from calcined bone showing the hydroxyapatite structure with the highest peak at $2\Theta = 31.8^{\circ}$

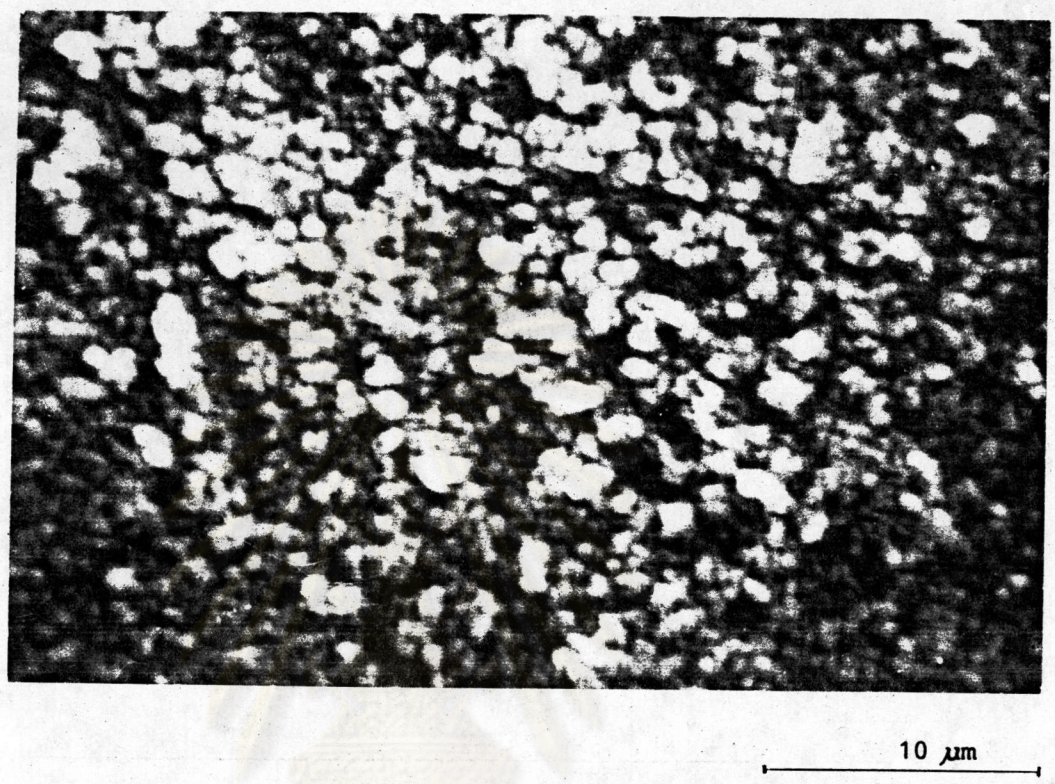

Fig. 2.3 Electron micrograph from powders in filter cake of calcined bone, x 7500

As may be seen, the very fine grain (~0.2 μm) and continuous pores indicated that material was not sintered at this stage.

2.2.2 Sintered materials

a) Phase

The recorded peaks observed correlated with the JCPDS powder diffraction file showed that the samples fired at 1100, 1200, 1250, 1300, and 1345° C completely composed of the hydroxyapatite and there was the indication fo the β - $Ca_3(PO_4)_2$ as a second phase from the samples fired at 1350° C (as seen from Fig. 2.4 at 2 θ : 31.5°). The higher the temperature is, the larger the amount of the second phase becomes (Fig. 2.5).

b) Microstructure

Fig. 2.6 demonstrated that the degree of sintering increased as the temperature was raised. Thus pores became isolated and disappeared at the grain boundaries and grain growth continuously occured. The grain sizes of materials sintered at 1250, 1280, 1300 , and 1345° C were approximated 0.6, 2.5, 5, 6 μm, respectively. FIg. 2.7 showed that the grain size at 1250° C, 3 hour-duration time was about 2 times larger than that received at the same temperature and 0.5 hourduration time.

c) Bulk density and apparent porosity

Fig. 2.8 - Fig. 2.9 showed the influence of temperature on densities and porosities of the different fired samples, and Fig. 2.10 - Fig. 2.11 showed the effect of time on these values. As may be seen, at the beginning of applying a constant

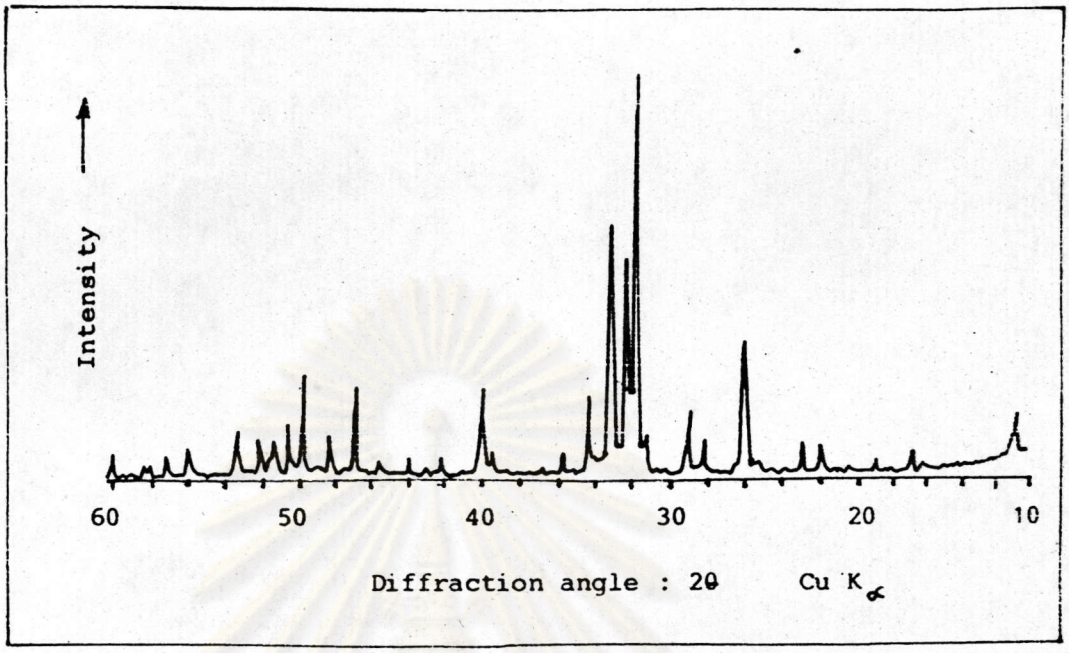

Fig. 2.4 X-ray diffraction peaks of hydroxyapatite fired at 1350° C for 0.5 hr showing the peak of β -$Ca_3(PO_4)_2$ as a second phase.

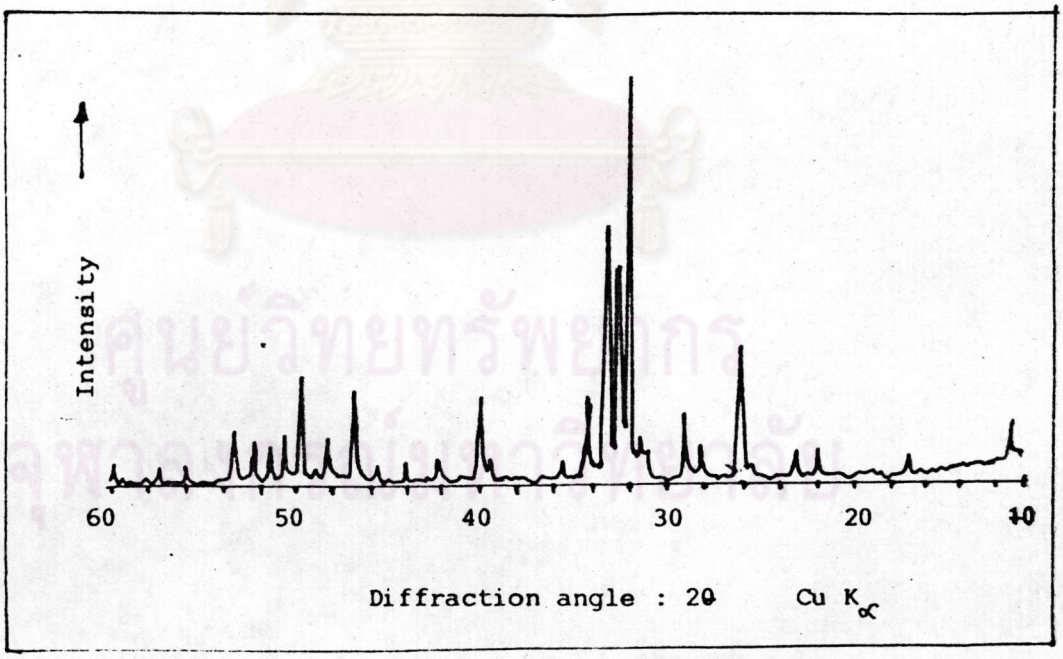

Fig. 2.5 X-ray diffraction peaks of hydroxyapatite fired at 1360° C for 0.5 hr

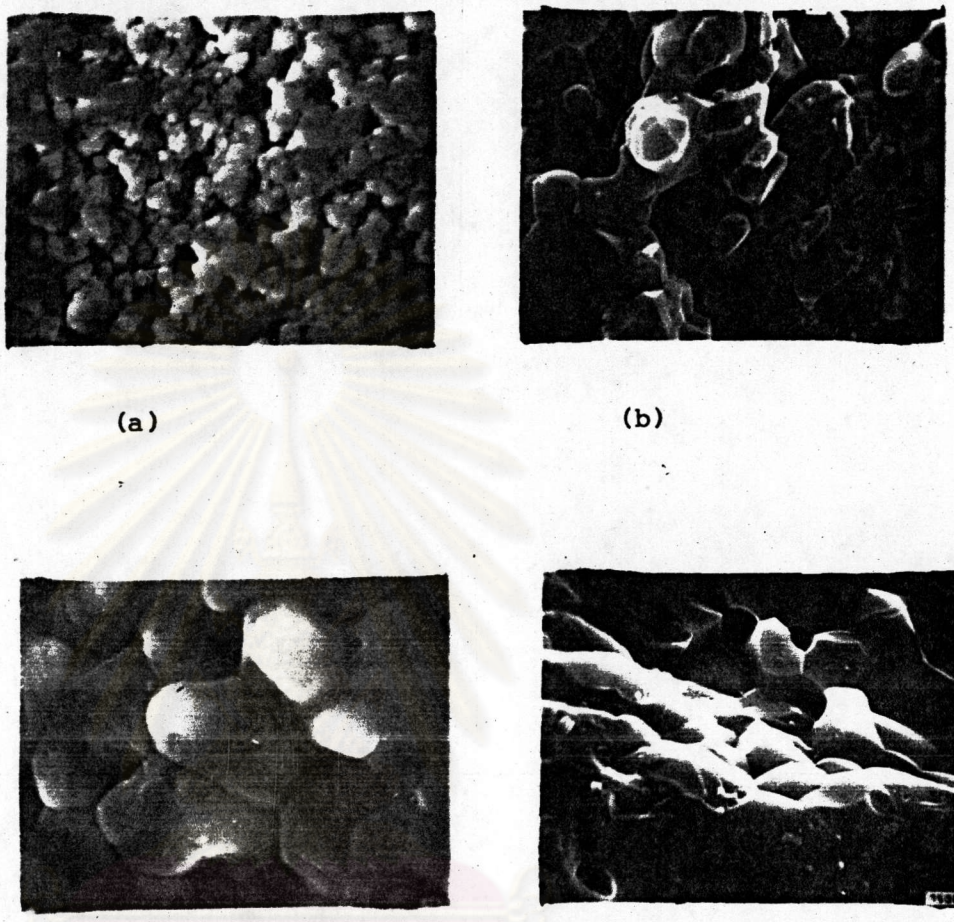

Fig.2.6 Electron micrographs of hydroxyapatite fired for 0.5 hr at (a) 1250° C, (b) 1280° C, (c) 1300° C, and (d) 1345°C., (x 7500)

Fig. 2.7 Electron micrograph of hydroxyapatite fired at 1250° c for 3 hrs., x 7500.

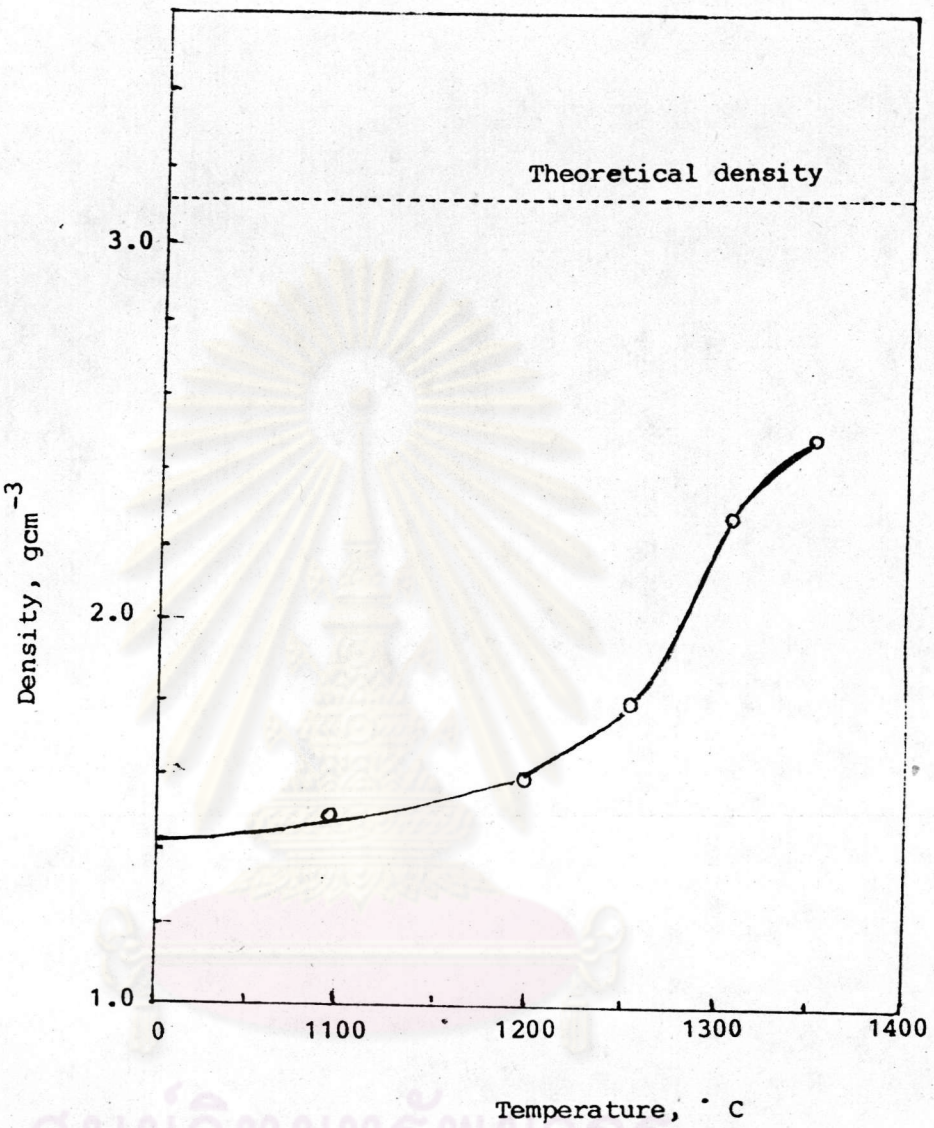

Fig. 2.8 Effect of temperature on density of hydroxyapatite

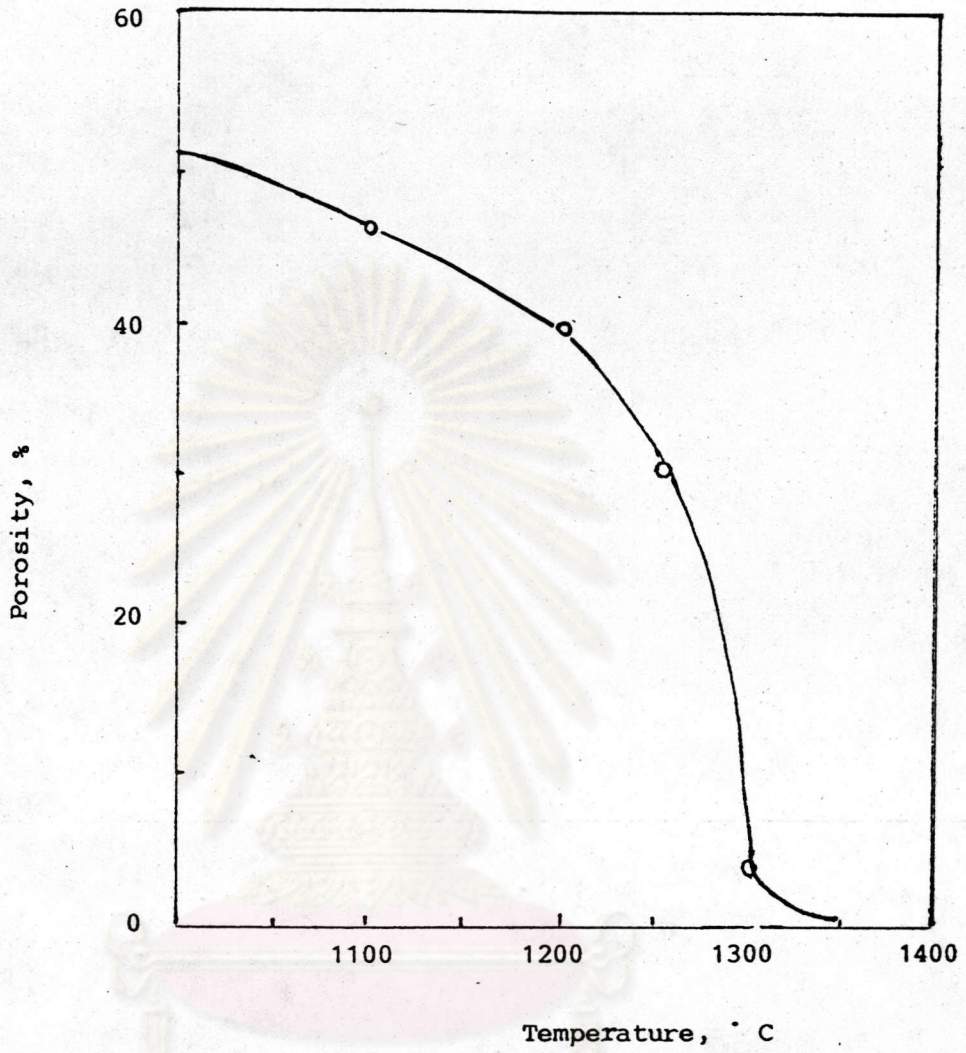

Fig. 2.9 Effect of temperature on porosity of hydroxyapatite

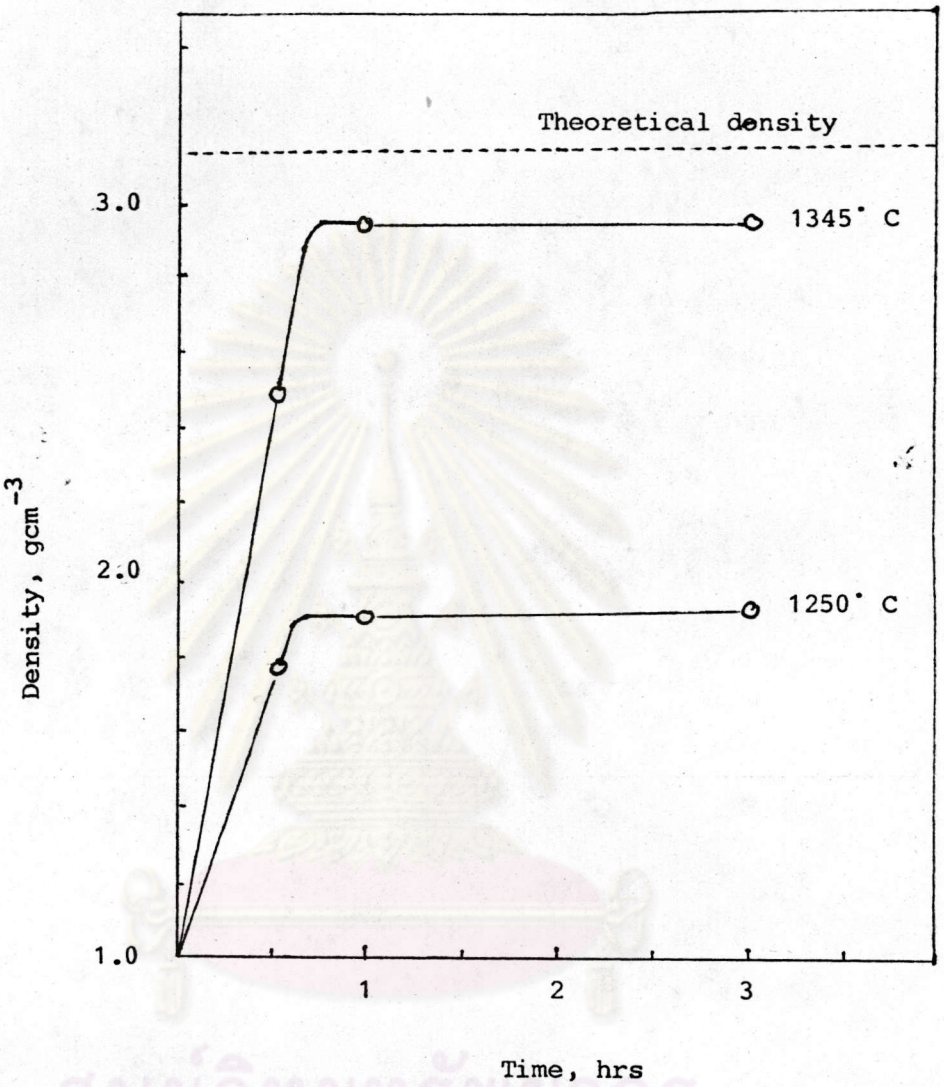

Fig. 2.10 Effect of time on density of hydroxyapatite

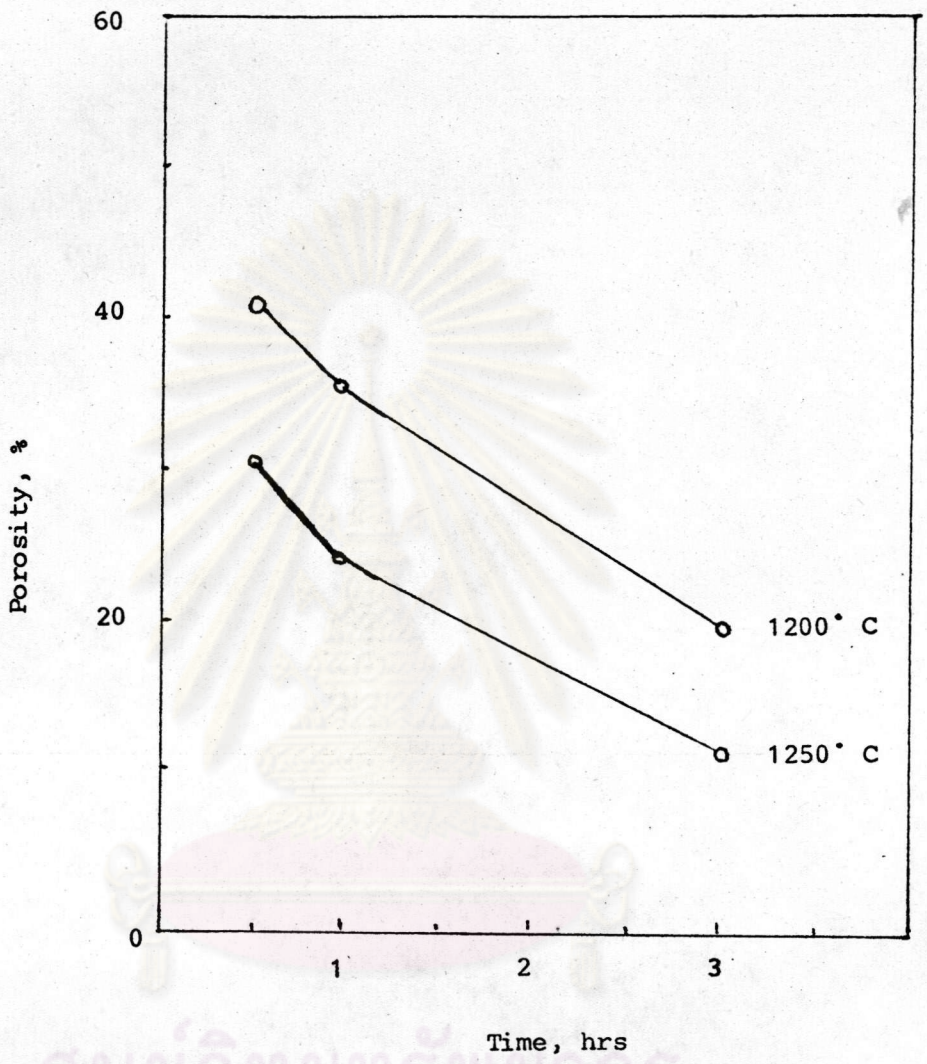

Fig. 2.11 Effect of time on porosity of hydroxyapatite

temperature, the density increased as a function of time, but for prolonged heating there was no significant change in this value. A terminal density achieved from sample fired at 1345° C for more than 1 hr was computed to be 94.2 % of the theoretical density of the apatite which was assumed to be 3.12 gcm^{-3} (14)
In contrast, the porosity was found to decrease with increasing temperature or/and time.

Of those sintered materials, the samples fired for the same duration time at 1250° C and 1345° C are selected to be the test materials using in indentation - controlled strength tests. Because both of them are completely hydroxyapatite and the former is representative for fine - grain porous specimens, and the latter for coarse - grain nonporous ones (see Fig. 2.12).

2.3 Discussion

It is technically accepted that the densification of the compacts into strong, useful ceramic components depends not only on a source of energy to activate and sustain the material transport presented during the densification, but also a variety of condition that can occur during processing (15). It is explicited that the normal sintering, which is the most common method for densification and is the convenient method for use in this study, do not result in achieving a cattle bone material in dense polycrystalline form. Undesired effects on material properties which increase reject products are also found, for example, irregularity in shape, formation of cracks and fracture surfaces. To overcome these effects the following factors, which can be the

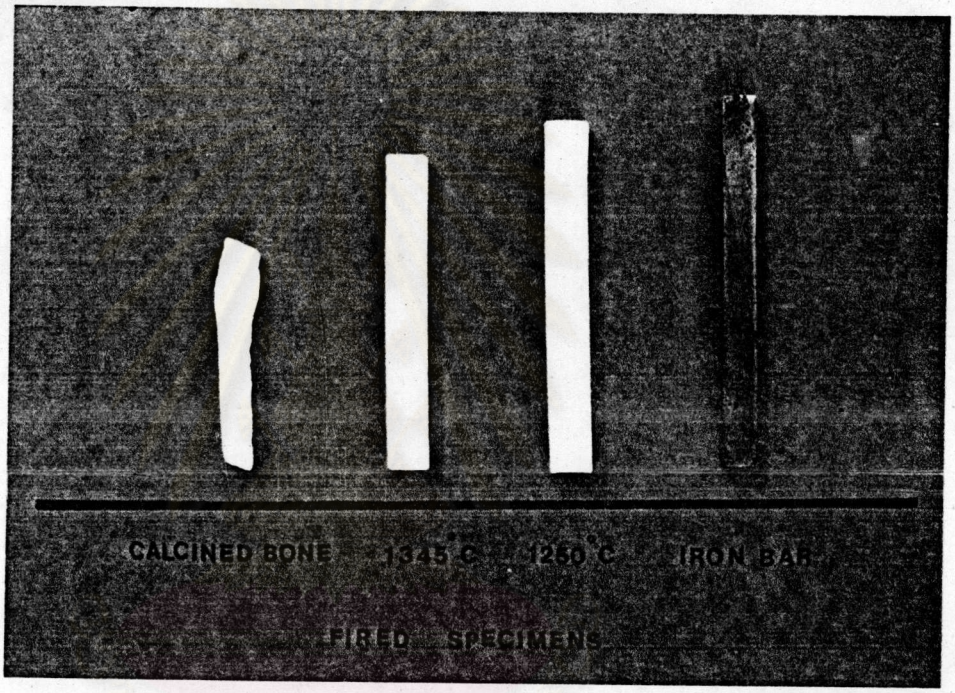

Fig. 2.12 Illustration of a piece of calcined bone, the bars of cattle bone material, and the iron bar. Variations in size of of different fired specimens are shown relative to the size of the iron bar.

sources of sintering problems, should be recognized and controlled : the burn - off of binders if large percentage or aggregate are present, thus the homogeneous mixing between proper binders and powders in suitable ratio are necessary ; too - rapid and non - uniform heat diffusion in materials which can be delayed by surrounding the compacts with alumina powders before firing (alumina powders are still stable at the temperatures below 1400° C) ; the non - uniformity of pressure applying which can be ignored in the case the automatic press is available for use , etc.

However, the energy available for densification can be increased by any other methods such as hot pressing which is analogous to sintering except that pressure and temperature are applied simultaneous resulting in reduced densification time and residual porosity whereas excessive grain growth does not occur.