CHAPTER 9

FABRICATION OF DENSE NANOCRYSTALLINE HYDROXYAPATITE CERAMICS FOR CRANIOTOMY FLAP FIXATION

Overview - Hydroxyapatite (HA) nanopowder was prepared from natural bovine bone by vibro-milling method with 4 h milling time. The nanocrystalline HA is designed as a button to reattach the bone flap after a craniotomy procedure. Each device is comprised of an inner plate and an outer plate. The fabrication processing was used the powders compression and then pressureless sintering at 1200°C for 3 h by rate-controlled sintering. The devices have fracture toughness (K_{1C}) values of 1.8±0.1 MPa.$m^{1/2}$. The nanorods pull out and liquid phase sintering of this sample contributed to the high fracture toughness that can be use as craniotomy flap fixation.

9.1 Introduction

During the past 50 years, bioceramics, especially hydroxyapatite (HA) have made significant contribution to use in biomedical industry for improving the quality of human life[3]. These ceramics are preferred as bone grafts in hard tissue engineering because of their superior biocompatibility and bioactivity[3]. Unfortunately, a HA ceramic is limited in its use[2-6], since its mechanical properties are not sufficient for more demanding load application, such as fracture fixation, artificial bone and tooth. Improvement in mechanical properties of HA, especially, the improvement in fracture toughness, is necessary for load bearing application[23,44]. Because of fracture toughness is important parameter required for the prediction of the mechanical performance of structural materials. Lopes et al in 1999[16] show the fracture toughness of the HA composite materials was mainly governed by the decrease in flaw size. They shown the evident that higher strength of HA composite should be mainly controlled by fracture toughness. Suchanek et al 1997[5] have also been reported, if the fracture toughness increase, the average strength and the Weibull modulus both increases. Consequently, the strength of the material becomes fewer flaws sensitive. Many experimental methods have been proposed to estimate fracture toughness. The indentation microfracture method, which yield for the mode I critical stress intensity factor, K_{1C}, is particularly useful when applied to brittle materials with low K_{1C}, since it is simple, fast and requires small testing areas[16].

Recently, nanoscale particle of HA (~10-100 nm) have received much attention studied by various researchers to overcome the existing limitations of hydroxyapatite, as well as to fabricate nanostructured scaffolds to mimic structural and dimensional details of natural bone[2-3]. It is reported that nanocrystalline HA can improve sinterability and densification due to greater surface area, which could improve the fracture toughness and other mechanical properties[3]. Nanoscaled HA is also expected to have better bioactivity than coarser crystals[3,30-31].

In our previous work, we have found that a rate-controlled sintering technique can be use for producing dense nanocrystalline HA ceramics in pressureless sintering. In this work, we have developed a simple process of preparing nanocrystalline HA ceramics to use as the craniotomy flap fixation. The fracture toughness and microstructure of the devices were also investigated.

9.2 Experimental procedures

The hydroxyapatite powder was derived from natural bovine bone by sequence thermally processes. The fresh bones were cut into smaller pieces and cleaned well to remove macroscopic adhering impurities. The bone samples were boiling in distilled water of 8 h for easily removes of the bone marrow and tendons. After that the bone has been deproteinzied by continued boiling in water. The boiling treated bone samples were dried overnight at a temperature of 200 °C. The deproteinized bone was calcined at 800°C for 3 h, with in this temperature no prions or any disease-causing agents can survive. The resulting product was crushed into small pieces and milled in a ball mill pot for 24 h. 20 g of dried powders were reground by vibro-milling method with milling time of 4 h. The phase identification of as-prepared powders have been examined via X-ray diffraction (XRD: Philip X’pert) techniques. For the microstructural analysis, the nanopowder sample was ultrasonically dispersed in ethanol to from very dilute suspensions and then the dried powder were mounted on stubs, gold-coated in vacuum and viewed under scanning electron microscope (SEM:JSM-6335F).

The nano HA powders have been pressed into pellet shape by uniaxial pressing with pressure of 50 MPa. The circular green HA disks were perforated at the center as to form the button shape. The simplest sintering method was used pressureless sintering at temperatures of 1200°C for 3 h by rate-controlled sintering (see Fig 9.1). Density and open porosity of the sintered samples was measured by the Archimedes’ method with distilled water as the fluid medium. The microstructure and fracture surface analysis of sintered HA ceramics were carried out by using scanning electron microscopy.

Fracture toughness (K_{1C}) was determined by an indentation technique as Anstis' equation[16,21-23]:

$$K_{1C} = 0.016\left(\frac{E}{H}\right)^{1/2}\frac{P}{c^{3/2}} \qquad (9.1)$$

Where *c* is the crack length (m), *E*, the Young's modulus (GPa), *H*, the hardness(GPa), *P*, the load applied (N).

A 9.8 N load was applied for 15 s using a pyramid shaped diamond indenter was indented 20 times. These indentations were also used to determine hardness.

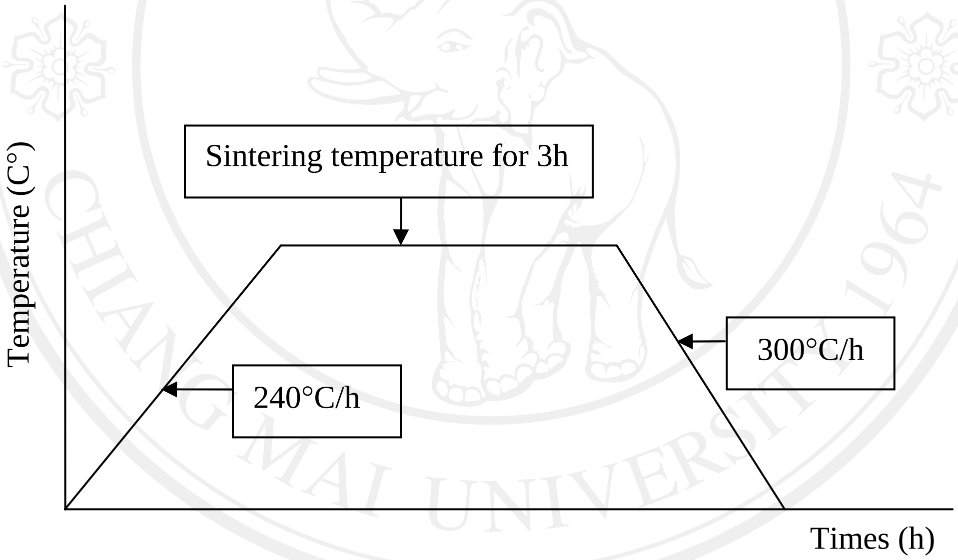

Fig. 9.1 Sintering program.

9.3 Results and Discussions

Fig. 9.2 shows the SEM micrographs of the nanoneedle-like structure of HA prepared from natural bovine bone after 4 h vibro milling time. The HA nanoparticles had a unifrom morphology with diameter less than 100 nm. The crystalline phase of the HA nanopowder was investigated by XRD only HA phase was found in the XRD pattern of nanopowder as shown in Fig. 9.3, indicating good crystallinity and high purity.

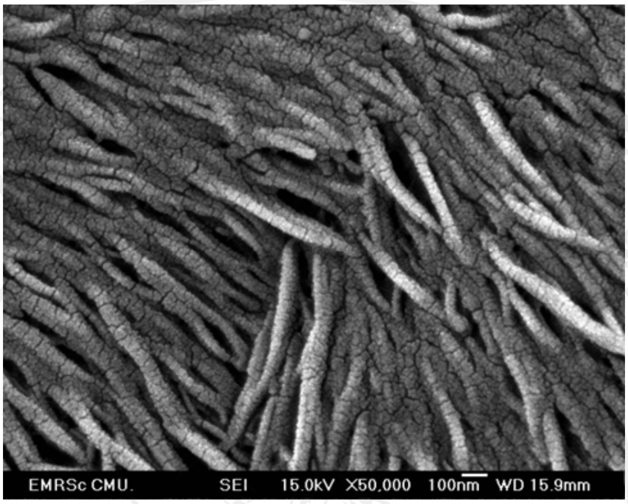

Fig. 9.2 SEM micrographs of nanoneedle-like structure of HA.

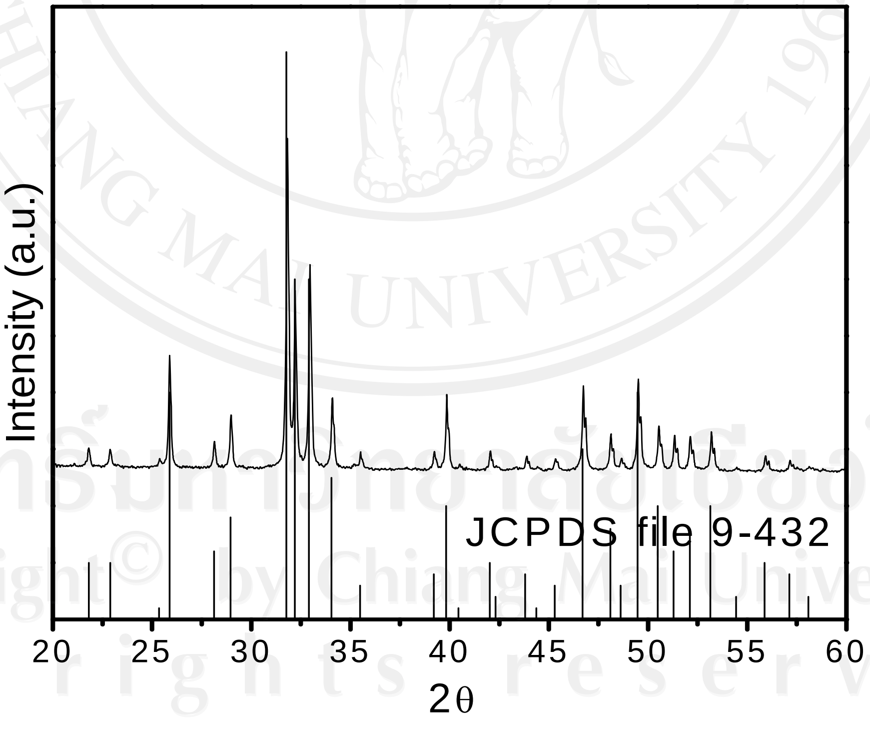

Fig. 9.3 XRD pattern of HA nanoneedle-like structure compared with JCPDS file 9-432 of pure HA.

Fig. 9.4 shows a representative optical photograph of a Vickers indentation obtained on the surface of samples sintered at 1200°C for 3 h. The cracks originating from the four vertices and diagonals of indentations were measured to K_{1C} and hardness determined. The fracture toughness result of sintered samples was 1.8±0.1 MPa.m$^{1/2}$ higher than that the average fracture toughness with 1 MPa.m$^{1/2}$ of pure microsized HA^{5}. Their bulk density was 95.2% (3.01±0.01g/cm^{3}) of the theoretical density of HA (3.16 g/cm^{3}).

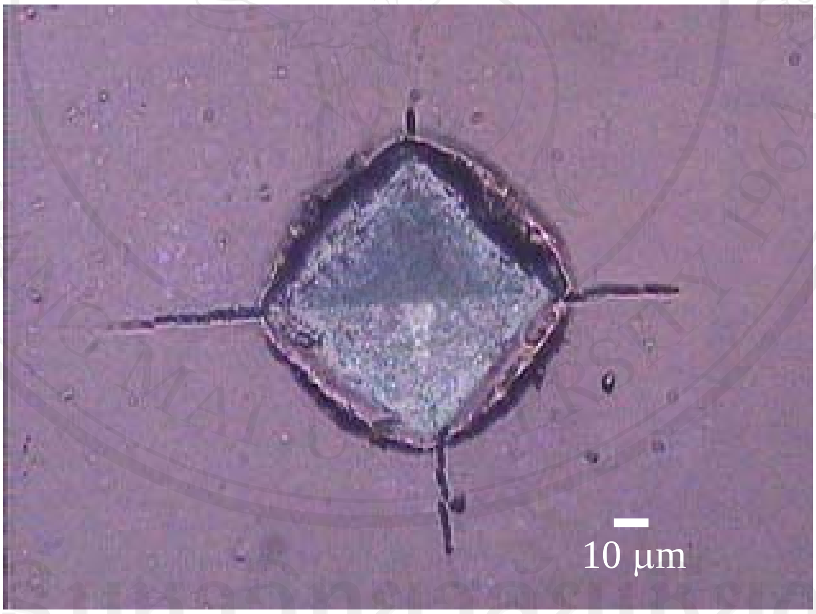

Fig. 9.4 Representative Vickers indentation obtained on the surface of sintered samples at 1200°C for 3 h.

The SEM micrograph in Fig. 9.5 reveal the fracture surfaces of the HA nanoceramics. The microstructure of nanocrystalline HA ceramics clearly show that it is no visible pores and proper densification. The occurrence of crack deflection bridging and pull-out phenomena of needlelike nanocrystalline HA and liquid phase sintering were observed in the microstructure. This indicates the improvement in the fracture toughness which suggests that crack bridging, crack deflection as a toughening mechanism[5]. Moreover, the liquid phase sintering increased the sintering densification rate has led to a phenomenon of superplasticity by grain-boundary sliding as the dominant deformation mechanism[30]. This phenomenon is as the result of low hardness 304.0±12.4 HV of sintered samples, it is lower compared to the large-grained HA ceramics. The low hardness values are expected to affect to an increasing toughness values in HA nanoceramics which corresponding to the fracture toughness resulted in this work.

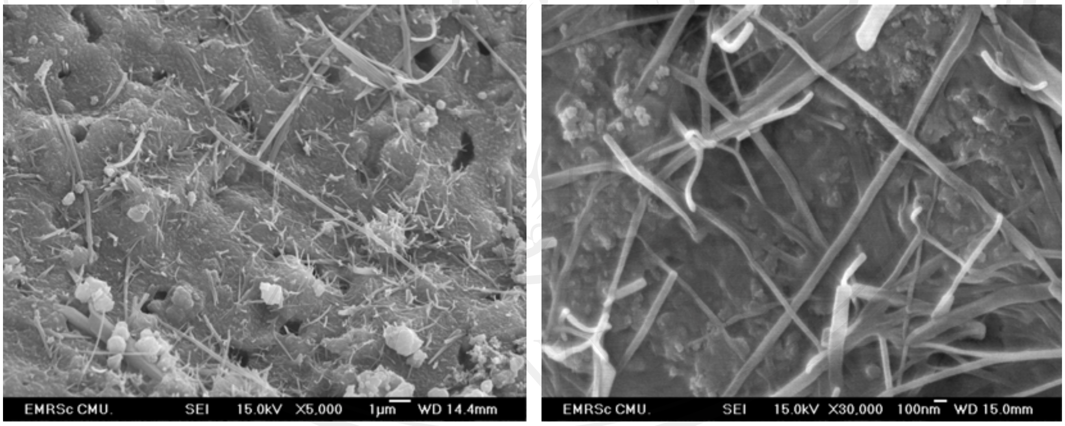

Fig. 9.5 SEM micrographs of fracture surface of samples: (a) low magnification and (b) high magnification.

The present study has shown a simple process that can be use to produce dense HA nanoceramic with high fracture toughness at a relative low temperature. The nanorod-shaped morphology could be retained in the final microstructure. Nanosized rod-shaped structure in sintered compacts can significantly improve fracture toughness and, therefore, improve other mechanical properties. Moreover, the occurred of liquid phase sintering by no sintering aid can improve grain-boundary properties of HA nanoceramic thereby higher increases fracture toughness. These materials have been designed as a dense button plates shape for reattaching the bone flap after a craniotomy procedure. The obtained samples are shown in fig. 9.6.

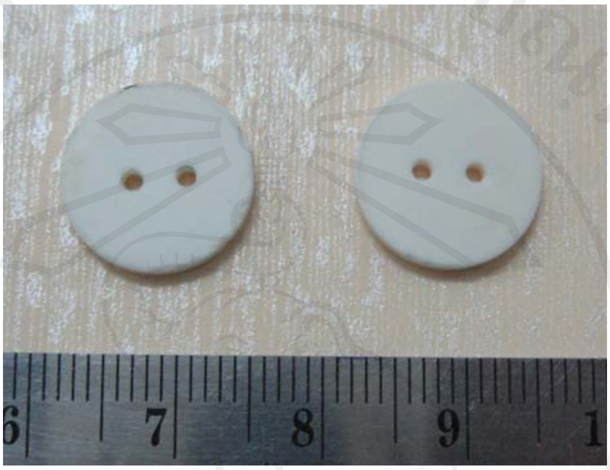

Fig. 9.6 Dense HA button, made from HA nanopowders (the scale shows centimeters)

9.4 Conclusions

The HA craniotomy flap fixation plates can be produce from the HA nanopowders. The simple sintering method was used pressureless sintering at relative low temperature made results of bulk density of HA nanoceramic more than 95% of the theoretical density. Fracture toughness of the sintered HA nanopowder reflected their microstructure and was the value of 1.8±0.1 $MPa.m^{1/2}$ higher than that the average fracture toughness of pure micronsized HA ceramics. The nanostructure with liquid phase sintering and toughening mechanisms of pull-out of nanocrystalline HA and grain boundary sliding of HA nanoceramic contributed to the increase of fracture toughness.