

CHAPTER 7

PROCESSING OF HYDROXYAPATITE NANOCERAMIC BY CONVENTIONAL SINTERING

Overview - Hydroxyapatite (HA) powders derived from bovine bone were milled in vibro-milling machine for 0, 1, 2, 4 and 8 h. It was observed that the nanocrystalline HA powder was started to form after using milling time of 2 h. The green compacted pellets of all HA powders were subsequently sintered at 1200 and 1300°C for 3 h and then the physical and mechanical characterizations as well as microstructural evaluation have been carried out. It was found that the optimum sintering temperature and milling time were 1200°C and 2 h, respectively, which gave the HA nanoceramic with the maximum bending strength of 69.3 ± 5.7 MPa and porosity of $21 \pm 0.07\%$. This is about 200% higher than that of the sample which made from micron sized HA powder, having similar porosity. The higher sintering temperature of at 1300°C resulted in the HA ceramic with poor strength due to the presence of glassy phase.

7.1 Introduction

The requirement of materials to replace or restore the function of traumatized, damaged, or lost bone is a major clinical need. Current therapies including autografting and allografting are good progress in bone grafting, despite they have limitation to some certain extent⁵. Recently, synthetic or naturally derived

hydroxyapatite (HA) is the most popular biomaterials for skeletal reconstructions, as it possesses excellent biocompatibility and osteoconductive properties and also forms a direct chemical bond with hard tissues²⁻³. Unfortunately, the HA materials cannot be used as heavily loaded implants because of their poor mechanical properties^{3,25}.

In the last few years the scientific community has gained very much attention in the potential of nanosized materials. Extensive studies by many researchers have indicated that the use of nanoscale ceramic powders improved sinterability and densification of the ceramics due to the high surface energy. Thus the nanocrystalline ceramics are able to exhibit improved toughness and other mechanical properties in comparison with the conventional polycrystalline materials^{3,30,51}.

Despite the high potential of using the nanoparticles in the HA ceramics, very few applications have been developed so far. The key limitation is the lack of large quantities of nanosized particles with closely controlled properties at a cost that will allow scientists and engineers to comfortably explore new practical applications of these particles as well as the science of processing these new materials. Therefore researchers should be focused on developing less expensive technologies for manufacture of nanoparticles that can be densified into nano-grain ceramics^{30,51}.

A number of techniques have been employed for producing HA nanostructural materials, such as sol-gel synthesis²⁰, co-precipitation²¹, hydrothermal reaction²², microemulsion synthesis²³ and mechanochemical synthesis²⁴, but most of them are limited to produce in small quantities. In the present work, we developed a simple vibro-milling method for forming the nanosized HA with a lower cost and the largely mass production. The mechanical properties and microstructures of the sintered samples were investigated comparing to their HA microceramic counterparts.

7.2 Materials and methods

The sample of hydroxyapatite (HA) nanopowders used in this work was obtained from natural bovine bone. The vibro-milling method was employed to obtain the nanopowder of HA phase as described in the previous report⁴³. The powders of 0, 1, 2, 4, and 8 h vibro-milling times were uniaxially pressed under a pressure of 50 MPa. Subsequently, they were sintered in an air atmosphere at 1200 and 1300°C with 3 h soaking time and a heating rate of 4 °C/min. Density and open porosity of the sintered samples were measured by the Archimedes' method with distilled water as the fluid medium. Phase and microstructural analysis of the sintered HA ceramics were carried out by using the X-ray diffractometer (XRD: XRD:Philip X'pert) and the scanning electron microscopy (SEM: JSM6335F), respectively. Hardness test was carried out in Vickers microhardness tester with major load of 0.98 N for 15 s. The flexural bending strength of the samples was obtained by ball-on-ring test method³⁴ using universal testing machine with constant crosshead speed of 5 mm/min. Six samples were tested and the average values were reported in all tests.

7.3 Results and Discussions

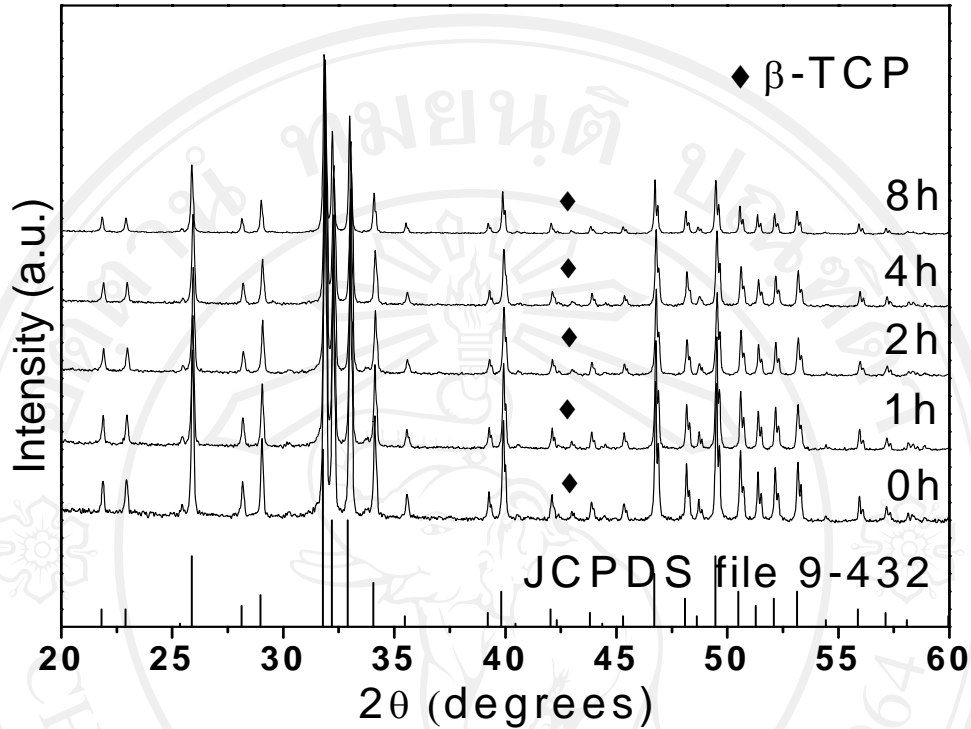


Fig. 7.1 X-ray diffraction patterns of various HA ceramics sintered at 1200°C for vibro-milling times (0-8h).

The XRD result of the sintered samples at 1200 and 1300°C is presented in

Fig. 7.1 and Fig. 7.2, respectively. It can be seen that the main phase of the ceramic samples is HA. Beta-tricalcium phosphate (β -TCP) were also observed in all sample sintered at 1200°C (Fig. 7.1), while in the samples sintered at higher temperature, i.e. 1300°C, additional α -TCP phase was found together with β -TCP (Fig. 7.2). This result indicates the more decomposition of the HA phase at the higher temperature. The values of density for the sintered samples as a function of vibro-milling time are shown in Fig. 7.3. The HA ceramics sintered at 1300°C have a higher value of density

than that of the HA ceramic sintered at 1200°C. Though the vibro-milling time is found to have insignificant effect on the densification of the HA ceramic, the optimum vibro-milling time must be in a range of 2-4 h.

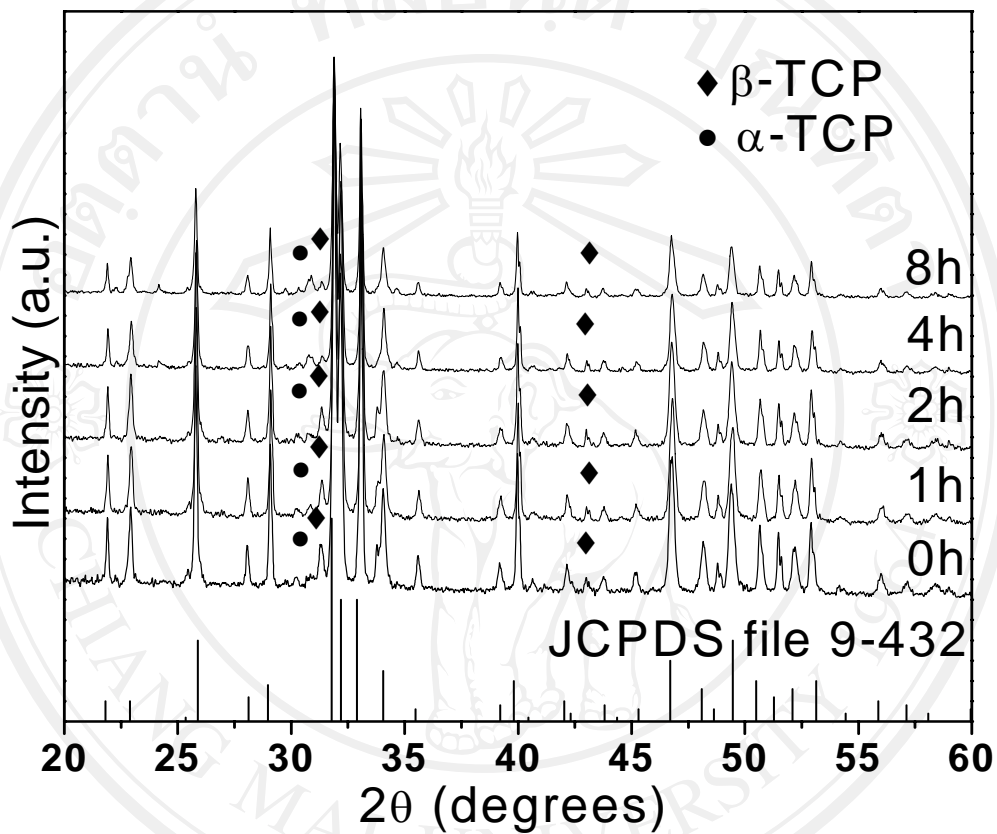


Fig. 7.2 X-ray diffraction patterns of various HA ceramics sintered at 1300°C for vibro-milling times (0-8h).

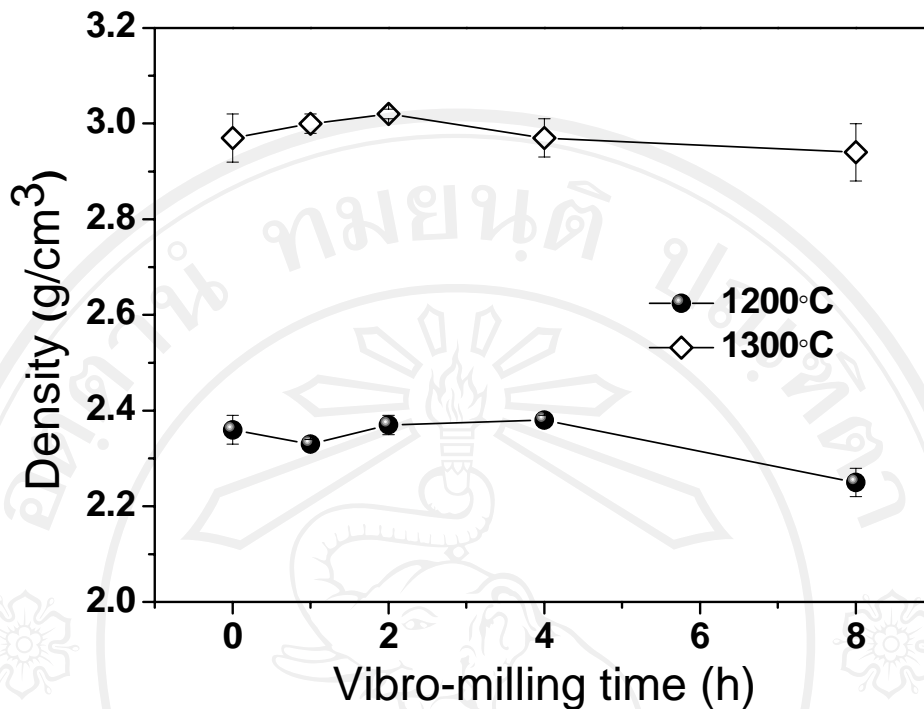
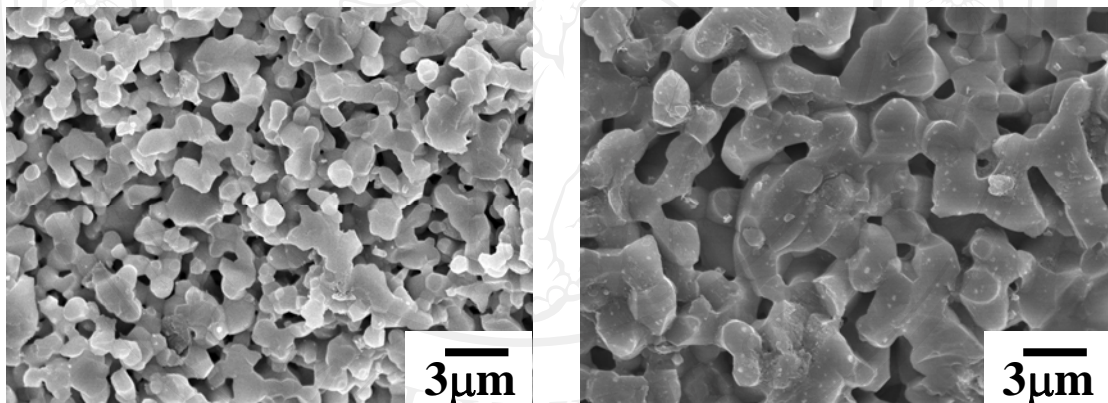


Fig. 7.3 Density as a function vibro-milling time for the HA ceramics sintered at 1200 and 1300°C.

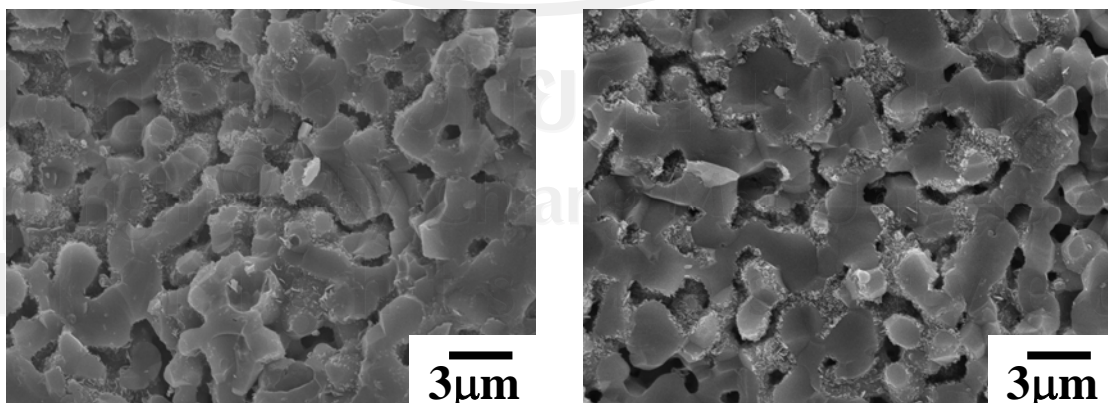
Fig. 7.4 shows the fracture surfaces of HA ceramics after sintered at 1200°C with different vibro-milling time. The densest structure was observed for the 2 h milling time sample (Fig. 7.4(c)) which agrees very well with the density data. The needle-like HA grains were also found to emerge from the surface of the nanosized grains in the ceramic samples using 2 h vibro-milling time as can be clearly illustrated in Fig. 7.5(a). This implies that the nanostructure of these HA particles could be retained at 1200 °C. The similar result of the nanostructure ceramic was observed in the sintered sample of 4 h milling time (Fig. 7.5(b)) but its microstructure had lower densification with high porosity as shown in Fig. 7.4(d). However the sintered sample with 8 h milling time, has excessive grain growth with micrometer needle-like HA

grains therefore no nanoscale morphology could be retained in its microstructure (Fig. 7.4(e)). It can be noted that the formation of many pores in 1200°C samples is beneficial, as they would permit the circulation of the physiological fluid throughout them¹⁶. SEM micrographs in Fig. 7.6 of the ceramic fracture surfaces sintered at 1300 °C, showing the full liquid phase and have a glass-like fracture surface. At this point, it may be assumed that the sintering temperature of 1300 °C is not suitable for forming the nanocrystalline HA ceramic as it gave poor microstructure as well as unwanted β -TC and α -TCP secondary phases.



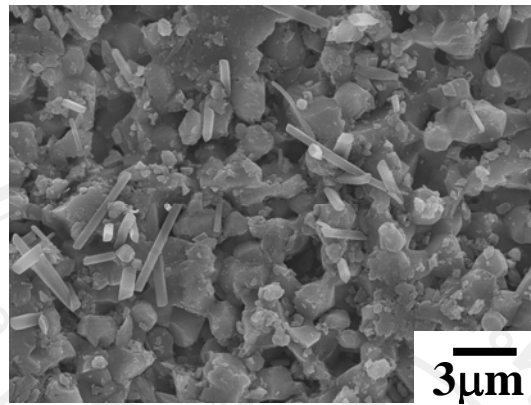
(a)

(b)



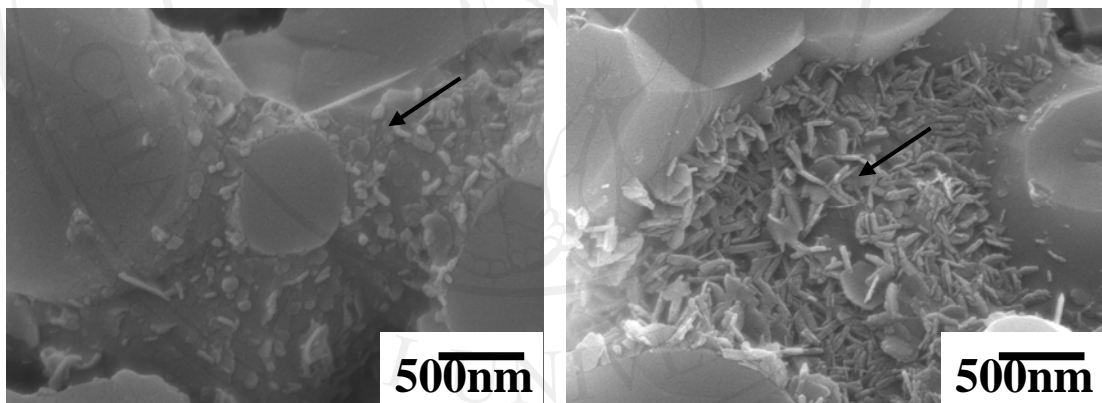
(c)

(d)



(e)

Fig. 7.4 Fracture surfaces of various HA ceramics sintered at 1200°C for various vibro-milling time; (a) 0 h, (b) 1h, (c) 2 h, (d) 4 h, and (e) 8 h.



(a)

(b)

Fig.7.5 Fracture surfaces of HA ceramics sintered at 1200°C for the vibro-milling times of: (a) 2 h and (b) 4 h. Arrows indicate the nanostructure HA grains embedded in the micron sized grains.

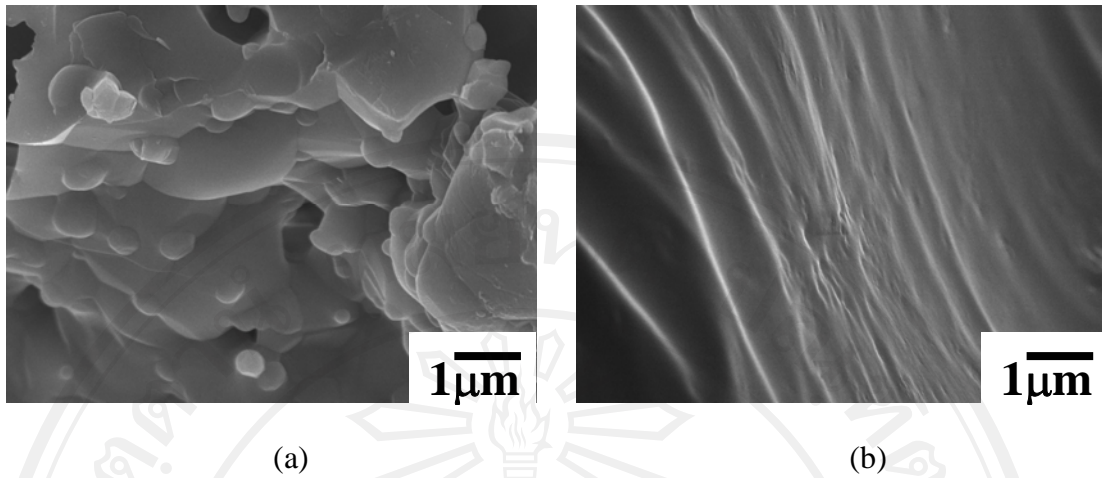


Fig. 7.6 Fracture surfaces of HA ceramic sintered at 1300°C; (a) 0 h, and (b) 8h.

Vickers hardness data as a function of vibro-milling time is shown in Fig. 7.7. In the samples sintered at 1300°C, there was a sharp increase from 474 HV to 605 HV for the sample with 0 h and 2 h milling time, respectively, and then the value decreased to 269 HV for the 8 h milling. For the lower sintering temperature at 1200°C, the hardness value increased exponentially with vibro-milling time. The higher values of hardness in the samples sintered at 1300°C can be related to the density effect, i.e., the higher density samples exhibits higher hardness value¹⁶. Fig. 7.8 shows the flexural bending strength versus milling time. For the samples sintered at 1300°C, the maximum flexural bending strength (54.9 ± 5.8 MPa) was observed for the 1 h milling time sample, while that of the samples sintered at 1200°C was found at 2 h milling time sample with the average value of 69.3 ± 5.7 MPa. This value is about 200% higher than that of the sample which fabricated by micron sized HA powder having similar porosity and sintered at the same temperature (34.9 ± 2.7), moreover this value is also close to the range of the values found for the cortical bone of rabbit femur (88 ± 20 MPa), which is an often used animal model⁷. It can be noted that the

lower strength of the 1200°C sample milled for 4 and 8 h, can be related to the high porosity as observed by SEM (Fig. 7.4 (d) and (e)). Consequently, it can be assumed that the nanoscale HA ceramics possess the higher strength overcoming that of the micron scale HA ceramics.

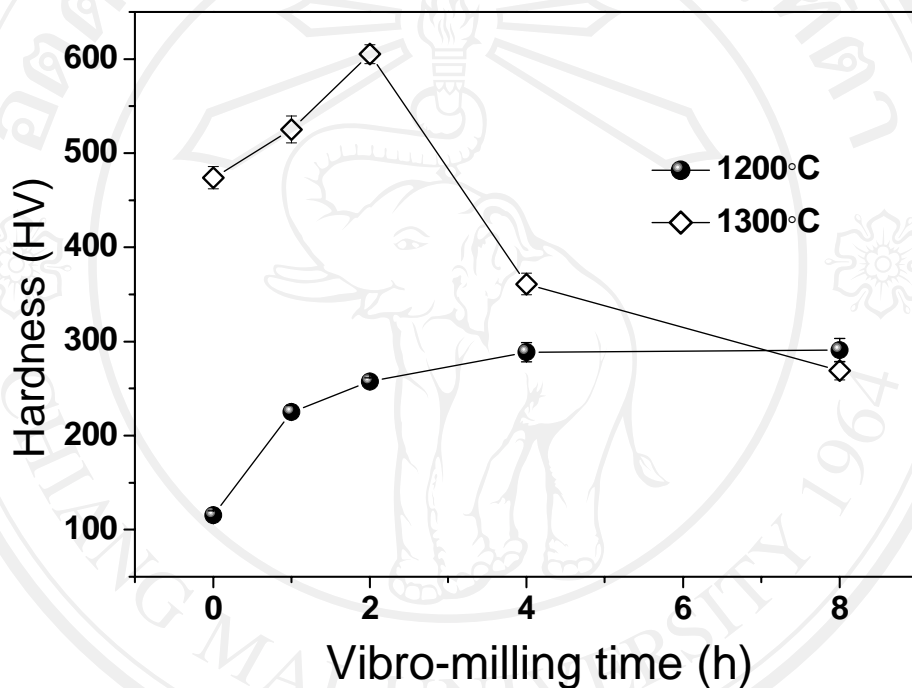


Fig. 7.7 Effect of vibro-milling time on Vickers microhardness of the HA ceramics sintered at 1200 and 1300°C.

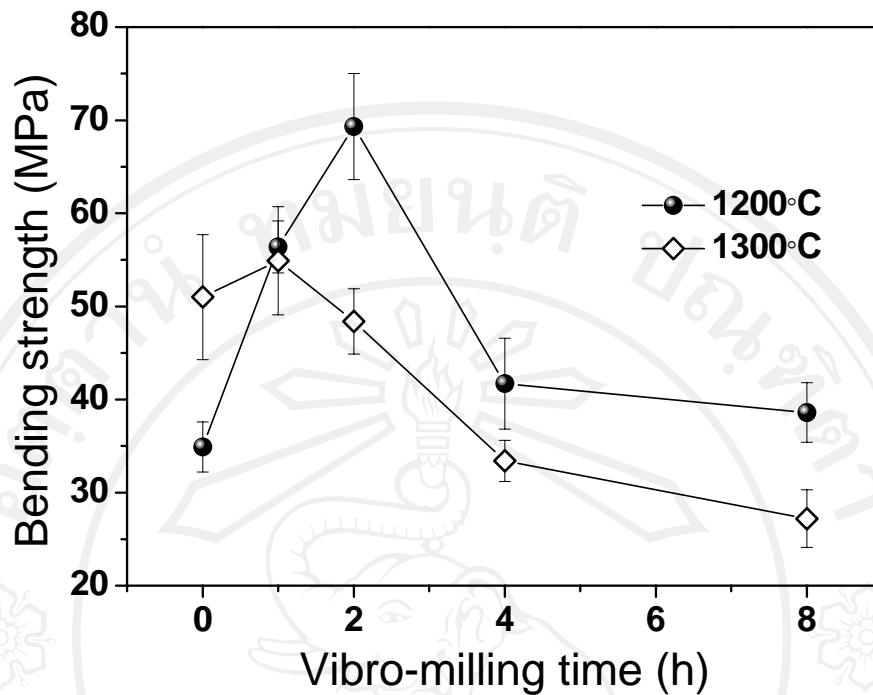


Fig. 7.8 Effect of vibro-milling time on flexural bending strength of the HA ceramics sintered at 1200 and 1300°C.

It was stated in the literature that critical sintering temperature for HA is 1300°C¹⁴ and above this temperature HA structure collapsed. In this work, we found that the resulted strength of the sintered HA nanoceramics at 1300°C is poor comparing to their HA microceramics counterparts. This means that the optimum sintering temperature for nanoscale HA ceramic is lower than that of the conventional HA ceramics. Therefore, the optimum sintering temperature for fabrication HA ceramics can be reduced by using the HA nanopowder as a starting material. However, because of the problem of agglomeration of nanoceramics powders made the low densification of HA nanoceramic in the samples 2 h and 4 h of milling times. This agglomeration lead to the poor sintering behavior though the individual

crystalline in the powders may be nano-sized, they are clustered together inhomogeneously that the powder compact contains micro-sized pores which are very difficult to eliminate during sintering. Therefore the agglomeration of nanoscale ceramic powders should be prevented or use the special technique for sintering that will be done in the next work.

7.4 Conclusions

In the present work, nanocrystalline HA ceramics were fabricated from the nanoparticles of natural bovine bone. The nanoparticles of natural bovine bone were obtained by using a vibro-milling method. The agglomeration problems are a limitation to high densification of HA nanoceramics. The maximum bending strength was achieved from the sample using 2 h vibro-milling time and sintered at 1200°C. This bending strength value is about 2 times higher than that of the sample which was fabricated by micron-sized HA powder having the equal amount of pores. The high porosity of this sample is expected to have great benefit to permit the circulation of the physiological fluid flow throughout such a scaffold device but the pore size is not enough for bone ingrowth.