CHAPTER 6

THERMAL STABILITY OF NANOCRYSTALLINE HYDROXYAPATITE POWDER

Overview - Hydroxyapatite (HA) nanopowder was prepared from natural bovine bone by vibro-milling method with 4 h milling time. Nanostructure of the resulting crystals had shown a uniform morphology and good crystallinity with diameter lower than 100 nm. The effect of heat treatment temperatures on phase stability and microstructure of the HA nanopowder were studied using X-ray diffraction and scanning electron microscopy. The decomposition of HA to β-tricalcium phosphate was occurred at 1150°C to 1250°C and future decomposition to α- tricalcium phosphate at 1300°C. SEM shows the powder was remained in nanoscales after heat treatment up to 1200°C.

6.1 Introduction

During the past 50 years, bioceramics, especially hydroxyapatite (HA) have made significant contribution to use in biomedical industry for improved the quality of human life[3]. These is the ceramic are preferred as bone grafts in hard tissue engineering because of their superior biocompatibility and bioactivity[2-6]. However, this bioceramics exhibits poor mechanical performance, which restricts their uses in load bearing applications[2-6]. It has been found that nanocrystalline HA powders offers approach to overcome the limitation of conventional HA materials[3]. Nanocrystalline

HA powders can improve sinterability and densification due to greater surface area, which could improve the fracture toughness and other mechanical properties[3]. Nano HA is also expected to have better bioactivity than coarser crystals[3]. However, sintering behavior of HA not only depends on particle size yet also on size distribution and morphology of the powder particles[28]. Additionally, in order to prevent HA powders from decomposing to tricalcium phosphate (TCP) at temperature above 900°C, the development of thermally stable, pure HA has become a significant issue for implant applications[12].

In our early work, we have found that a vibro-milling technique could be used for producing needle-like nanocrystalline HA powders in between 2-4 hours from natural bovine bone. Since the natural bone consists of plate- or needle-like HA nanocyrstals with dimensions of about 50–100 nm in length and 1-10 nm in diameter[24], therefore the mechanical action of vibro-milling method may provide a sufficient amount of kinetic energy to separate the HA single crystals from the bone scaffold and the optimum time spent results in better size and morphology distribution of the HA nanopowders. In this research, we have developed a simple process of preparing thermally stable in nanocrystalline needle-like HA from natural bovine bone. The effect of heat-treatment temperatures on phase stability and microstructure of the HA powder was investigated.

6.2 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 nanocrystalline HA powder were heat treatment in air at temperatures range between 1000 and 1300°C, at a heating rate of 4°C/min and soaking time of 3 h. The thermo-gravimetric analyser (TGA: TGA Mettler Toledo:TGA/SDTA 851e) was performed to analyze the phase transition in the temperature rang of room temperature to 1200°C. Microstructure evolution and phase stability were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

6.3 Results and Discussions

Fig. 6.1 shows the SEM micrographs of the HA nanoneedle-like structure prepared from natural bovine bone after 4 h vibro milling time. The HA nanoparticles had a unifrom morphology with diameter smaller 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. 6.2, indicating good crystallinity and high purity.

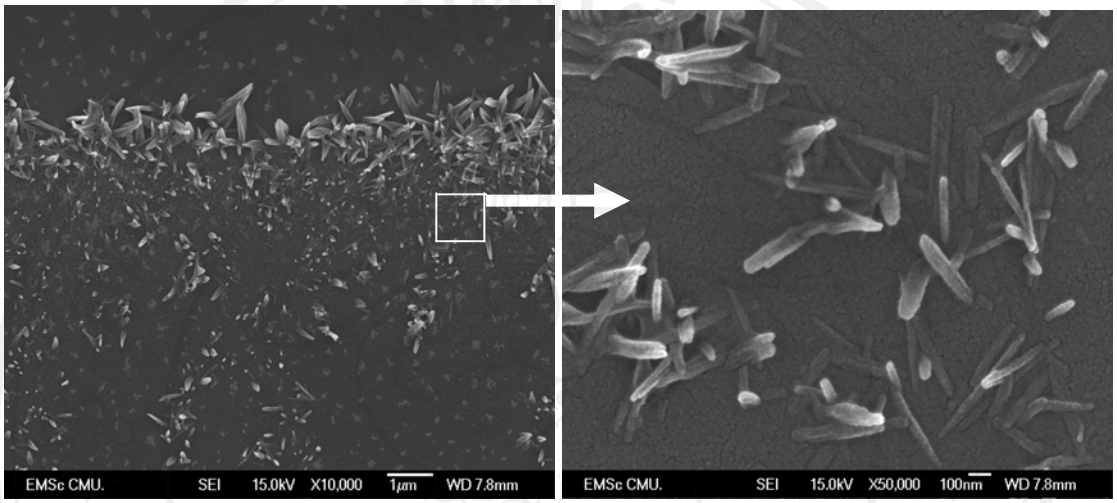

Fig. 6.1 SEM micrographs of HA nanoneedle-like structure.

The results of phase analysis by XRD of the heat treated samples at different temperatures are presented in Fig. 6.3. The XRD diffraction patterns of the samples heating below 1150°C contains only HA phase and no other phases were found in the pattern as all the peaks of the samples heated at 1000°C and 1100°C correspond with the JCPDS card No. 9-432 of HA phase. All samples heated from 1150°C onward revealed the presence of β-TCP peaks in their XRD patterns indicating that the decomposition of nanopowder started to occur at 1150°C and at 1300°C it further decomposed to form α-TCP phase. However, the presence of β-TCP peaks at 1150°C and 1200°C not occurred at the main peak, it can be assume that their have in small amount. These is correspond with TG-curve of the as-prepared HA nanopowder in the

temperature range of room temperature to 1200°C (Fig. 6.4.). An obvious weight loss about 0.4 and 1.2% was detected at 1150°C and 1200°C, respectively.

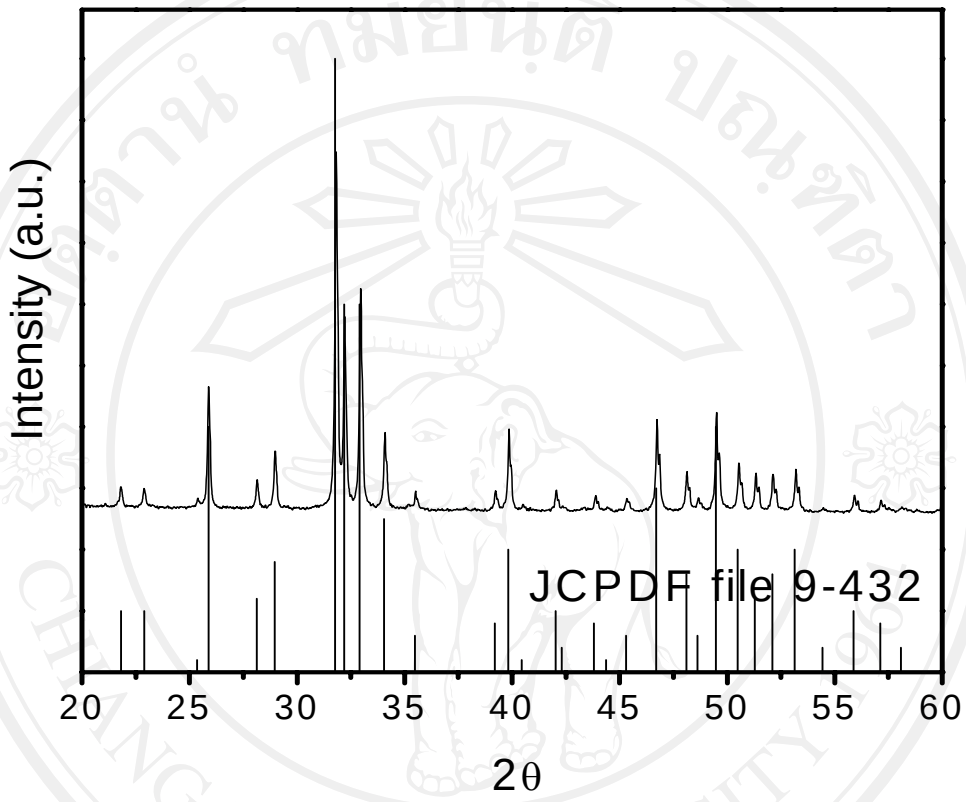

Fig. 6.2 XRD pattern of HA nanoneedle-like structure compared with JCPDS file 9-432 of pure HA.

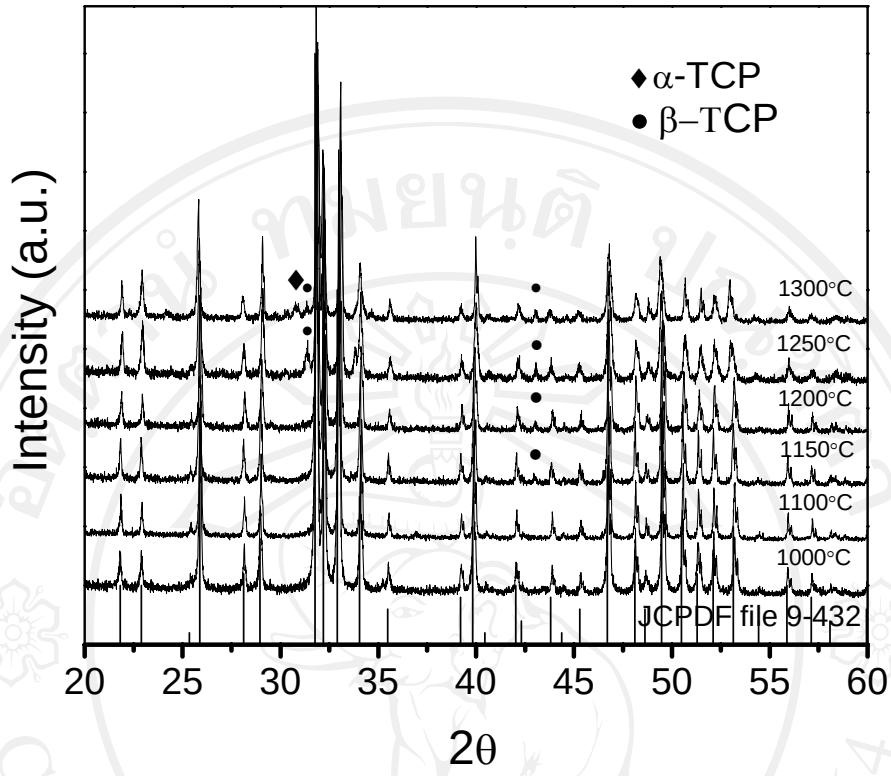

Fig. 6.3 X-ray diffraction patterns of nanocrystalline HA powders after heated at 1000°C, 1100°C, 1150°C, 1200°C, 1250°C and 1300°C compared with JCPDS file 9-432 of pure HA.

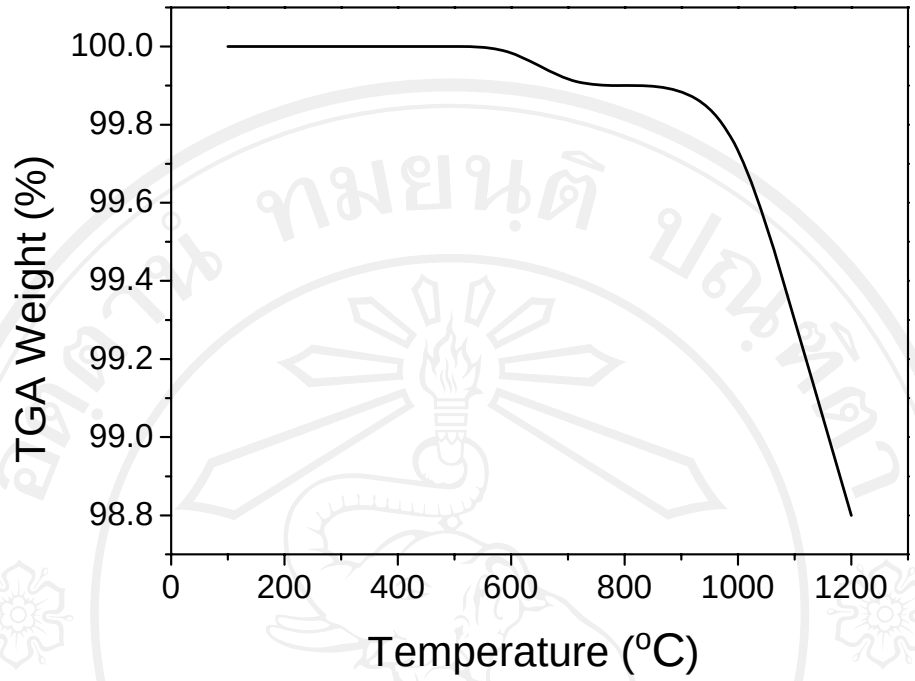

Fig. 6.4 TGA result of HA nanopowder.

Fig. 6.5 shows the SEM images of the nanocrystalline HA powders after heat treatment at temperatures range between 1000°C and 1300°C for 3 h. The coarsening of crystallites on heating was illustrated that the particles will approach each other closer due to the increased van der Waals force or due to presence of liquid phase within the granules. It can be seeing from Fig. 6.5(a) to (d), although the individual particle were loosely aggregated into spherulites but the grain size of HA remain lower than 100 nm. In Fig. 6.5(e) and (f) clearly shows occurs full liquid phase of nanoscaled HA crystals on heating at 1250°C and 1300°C.

The above results show that vibro-milling method can separate the nano HA crystals from natural bovine bone scaffold. The microstructure and phase stability of HA nanopowder depending on the heating temperature. The natural HA nanopowder

has thermal stability at 1100°C and can sintering up to 1200°C with only small change grain size which would be finally useful for specific application as mentioned before.

6.4 Conclusions

This vibro-milling method provides a simple route for prepared nanoneedle-like hydroxyapatite powder from natural bovine bone with low cost, reproductively and high mass productivity. The as-prepared is pure nanocrystalline HA powder and close to be the stoichiometric HA. The phases of nanocrystalline HA were stabilizing after heating at below 1150°C. The nanoscale grain size of HA seemed to be thermally stable up to 1200°C, and changed to the full liquid phase at 1250°C and 1300°C.

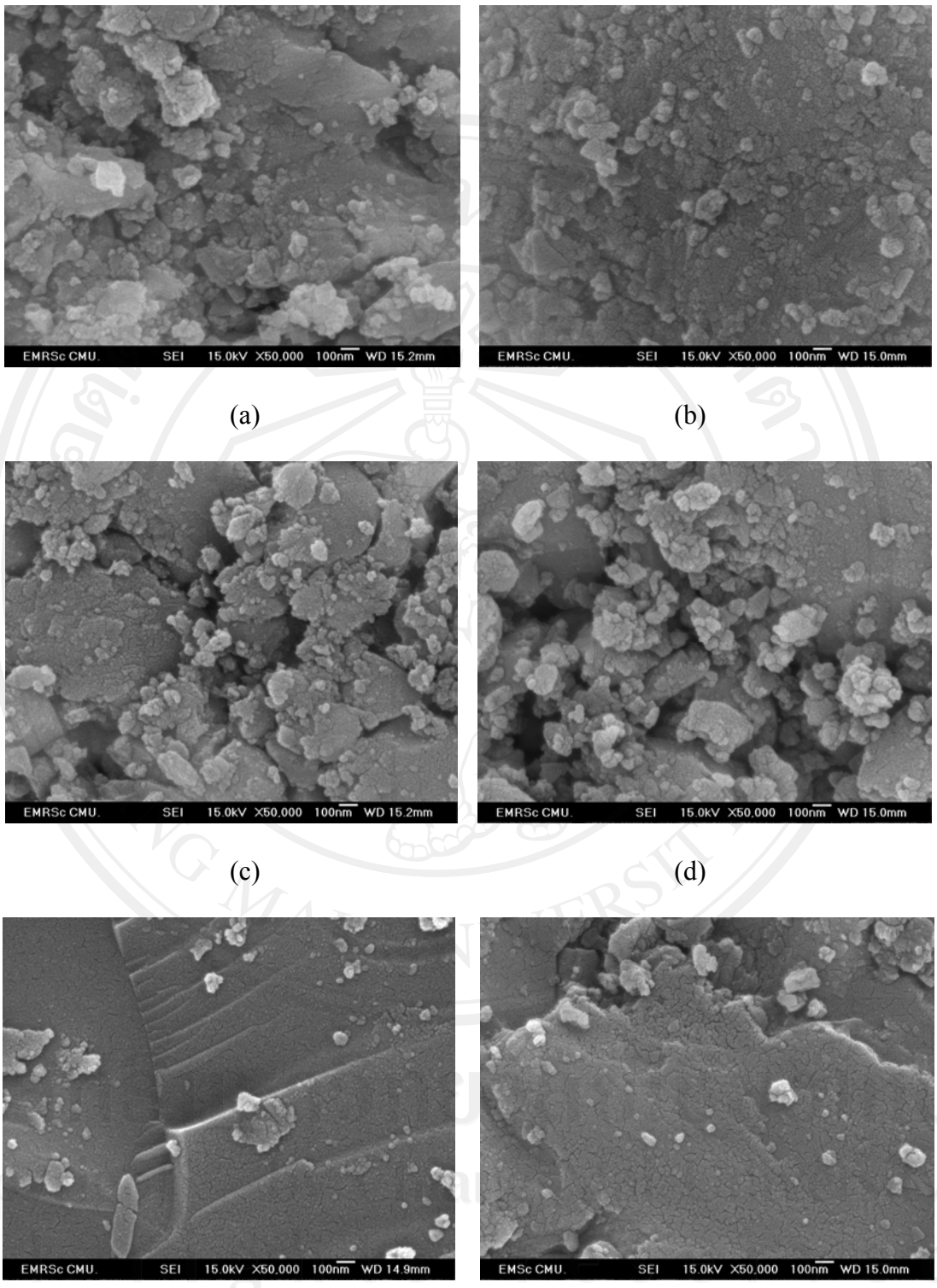

Fig. 6.5 SEM micrographs of nanocrystalline HA powders after heated at 1000°C:(a), 1100°C:(b), 1150°C:(c), 1200°C:(d) 1250°C:(e) and 1300°C:(f).