CHAPTER 8

ENHANCEMENT OF MECHANICAL PROPERTIES OF NANOCRYSTALLINE HYDROXYAPATITE CERAMICS BY RATE-CONTROLLED SINTERING METHOD

Overview - The rate-controlled sintering method combining with hydroxyapatite (HA) nanopowder was used successfully to prepare HA ceramic with enhanced physical and mechanical properties. The HA nanopowder was prepared from natural bovine bone via vibro-milling route. In comparison, both conventional and the rate-controlled sintering methods were employed for producing the HA ceramic at various sintering conditions. By using this rate-controlled sintering technique, the maximum values of bending strength of 88.6±3.0 MPa were achieved for the sample sintered at 1200°C. These values are closely similar to that of compact human bone and more superior than that found in HA sample using conventional sintering route. Additionally, the optimum sintering temperature of the rate-controlled method was less than at from conventional one. This rate-controlled sintering technique was firstly proved to be useful in producing the highly dense HA nanoceramic for bone graft applications.

8.1 Introduction

In the recent years, the arena of nanomaterials has been extensively applied in various fields because of their distinct properties compared with the normal materials.

In case of ceramics, most of researchers have focused on nanostructure of ceramics mainly involved the preparation of nanoceramics powders, such as engineering sized and shape of the high surface area nanoceramic powders. The distinct properties nanopowders offers final ceramic products of high the densification and mechanical properties [3,45,49].

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is a material showing an excellent biocompatibility and bioactivity with the human body [2-3,28]. This material is thus a most attractive material considerable interesting for the medical applications. The properties and method of preparation of HA are extensively studied by many research groups in the past[2,9,11,24,27]. HA has a hexagonal structure with the lattice parameter of a=b=9.42A and c=6.88A. The chemical properties of HA are close to the mineral constituent of human bone and the stoichiometric Ca/P ratio was 1.67[11]. It is reported that HA is a nanomaterial in its nature. HA nanoparticles, collagen fibers, and water are main constituent of natural bone[3]. Although HA shows very good biological properties, the mechanical properties of synthetic HA are rather poor compared to the natural human bone which restricts their applications at high load-baring areas. Much attention has paid on the improvement of the mechanical properties of this material for the reliability in really biomedical application. A way to solve the mechanical problem is to fabricate the HA ceramics by HA nanopowder due to it has a high surface area which expect to have a better densification. Therefore, HA nanopowder has been synthesized by many research groups with various methods such as sol-gel, hydrothermal and precipitation[3,45]. However, the main problem of ceramics nanopowder is the formation of agglomerates due to the interparticle boning and hindered packing, resulting that a formation of a hollow structure, an inomogeneities

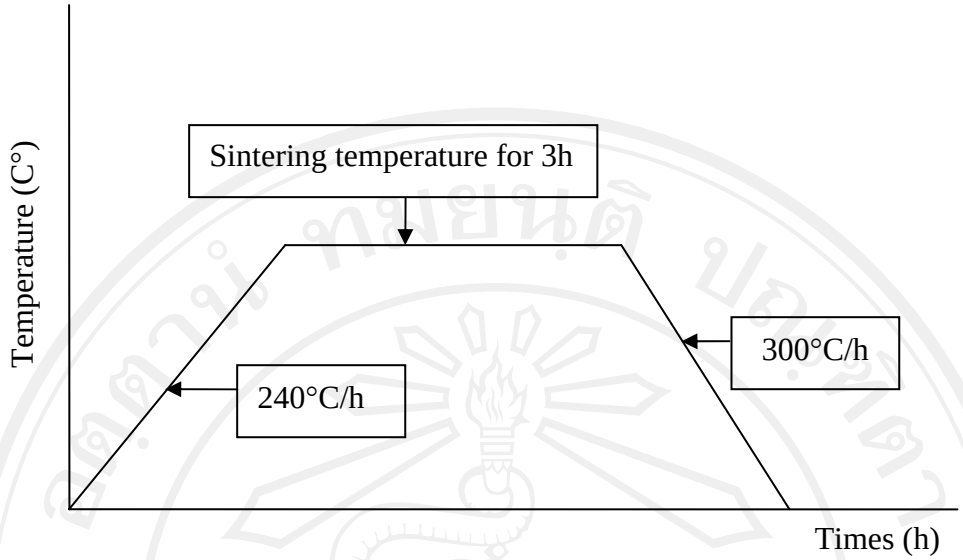
in packing and degrades sintering. Negative results in mechanical properties have been reported by many previous works who prepared the HA ceramics by HA nanopowders[28,31,45]. In order to solve this problem, some authors have fabricated the HA ceramics by using some special technique such as isostatic pressing, hot-pressing spark, and plasma sintering[45]. Conventional pressureless sintering is a most common low cost approach to sinter ceramics of nanopowders but it is difficult to realize densification without grain growth[31,45,51].

It is suggested from literatures that the rate control sintering method can be used to solve the agglomerates problem and improvement the densification of some ceramics prepared from nanopowders[4,30-31,49]. To our knowledge, rate control sintering method has not been applied in case of HA nanomaterial. Further, the properties of HA ceramics synthesized from HA nanopowder which derived from bovine bone have not been wildly investigated. The aim of the present work is to demonstrate an improvement of the mechanical properties of HA ceramics which fabricated from nanopowder of HA by using a rate-controlled sintering method. The HA nanopowders was derived from natural bovine bone. Results of densification and mechanical properties of the HA ceramics prepared by rate-controlled sintering method were compared to the normal sintering method.

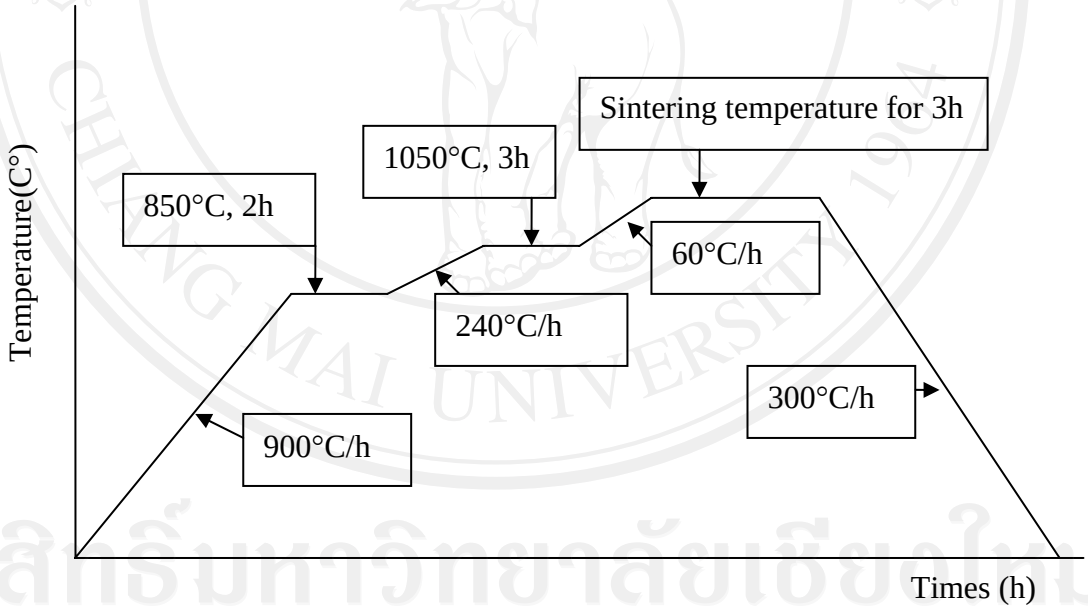
8.2 Experiment procedures

The hydroxyapatite powder was derived from extracted deproteinized bovine bones follow by heating at 800°C for 3 h. The obtained bones were crushed to small pieces and milled with ball milling for 24 h and then sieved to average particle size less than 45 μm. The powders were then milled by a vibro-milling method for 4 h.

The obtained powders were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The ceramics samples were prepared by pressing the powders into pellet shape using a uniaxial pressing with pressure of 50 MPa. Two methods were used to sinter the samples. For the first method, normal sintering, the green compacts were sintered with linear heating and cooling rate of 4 °C/min, Fig. 8.1 (a). In the second method namely rate-controlled sintering method, the green compacts were sintered with many steps as seen in Fig. 8.1 (b). The sintering temperature was varying from 1150°C, 1200°C, 1250°C and 1300°C for 3 h for both methods. Density of the sintered samples was 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 and the scanning electron microscopy, respectively. Hardness was determined by a Vickers indentation technique. A 9.8 N load was applied for 15 s using a pyramid shaped diamond indenter. The bending strength of samples was measured by a ball-on-ring test method[34] using universal testing machine with constant crosshead speed 5 mm/min. Six samples were tested and the average values were reported for all mechanical tests.



(a)

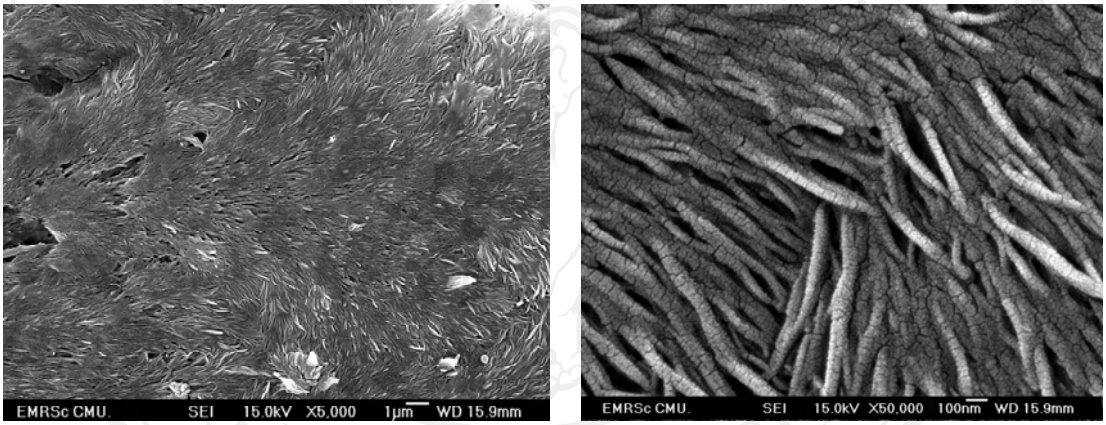


(b)

Fig. 8.1 Sintering programs for: (a) conventional method and (b) rate-controlled sintering method.

8.3 Results and Discussions

Fig. 8.2 (a) shows morphology of powder obtained from vibro-milling for 4 h. The powder exhibits needlelike shape with uniform distribution. However, agglomerate of particles was observed. In order to disperse the particle, the agglomerated power was dispersed by an ultrasonic bath with alcohol as a dispersion media. Fig. 8.2(b) shows the individual particles with diameter less than 100 nm. Therefore, the nanoparticle of HA could be obtained by vibro-milling method.



(a) (b)

Fig. 8.2 SEM micrographs of HA powders: (a) after vibro-milling, (b) after ultrasonic treatment.

The crystalline phase of the nanopowder was characterized by XRD as seen in Fig. 8.3. Indexing of XRD peaks was carried out according to the JCPDS file no. 9-432. The XRD analysis confirmed that the phase of the nanopowder is HA with no impurity or other phase. It is known that the properties of HA are strongly influenced on the Ca/P molar ratio. In This work, Ca/P molar ratio was determined by energy – dispersive x-ray analysis (EDS) The Ca/P molar ratio in the nanocrystalline was

analyzed to be as 1.66 which is closed to the theoretical value of the pure hydroxyapatite (1.67). In addition, there are no significant trace elements, confirming the high purity of nanocrystalline HA powder.

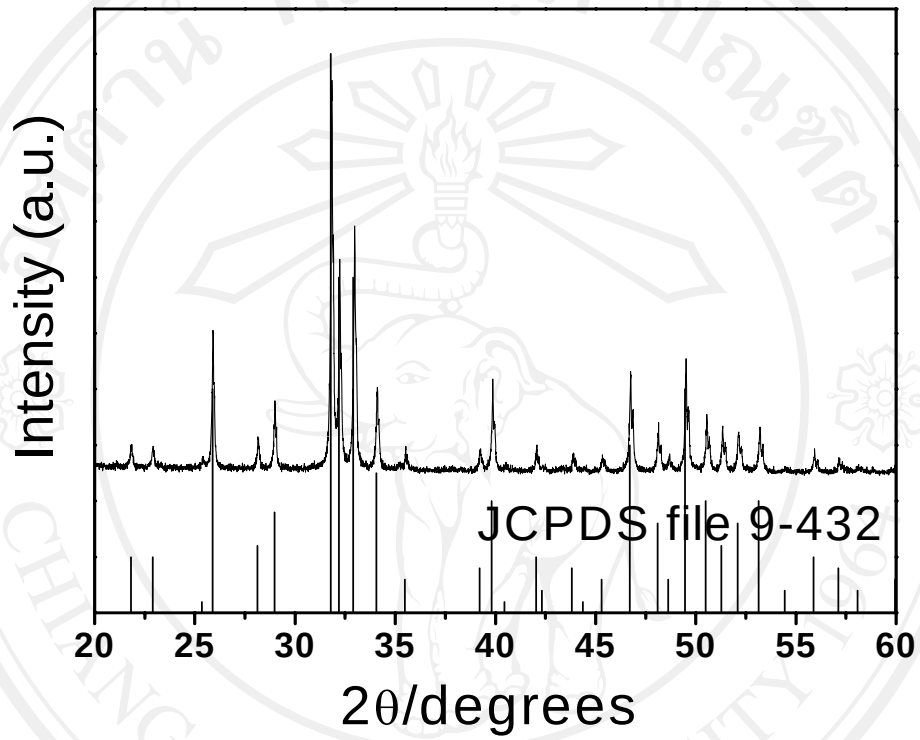
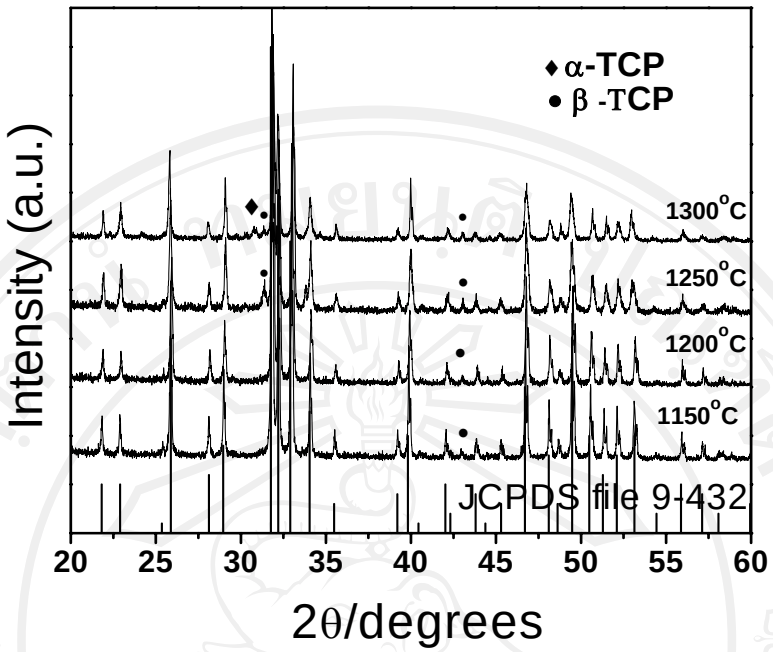


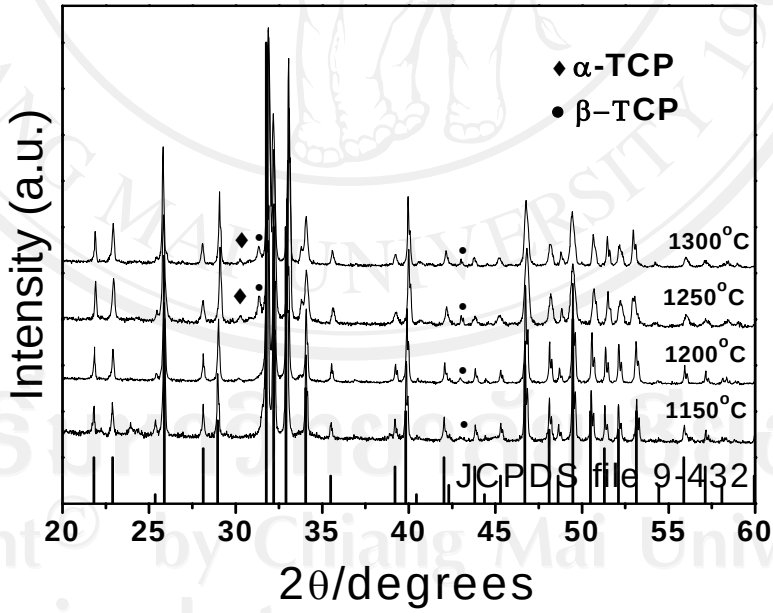
Fig. 8.3 XRD pattern of HA nanopowder.

In the present work, HA ceramics were fabricated at various sintering temperature by two methods, i.e. normal sintering and rate-controlled sintering methods as described in the experiment part. The phase formation of the HA ceramics was analyzed by XRD technique. XRD patterns of the HA ceramics prepared by the normal sintering method are shown in Fig. 8.4 (a). The result reveals that main phase of the ceramics is HA. However, Beta-tricalcium phosphate (β-TCP) was also found occurred for all samples after sintering. In addition, alpha- tricalcium phosphate (α-

TCP) was found in the sample sintered at 1300°C. A similar result was also found in the samples prepared by the rate-controlled sintering method as seen in Fig. 8.4 (b). In addition, the main XRD peaks of α-TCP and β-TCP were not observed but the minor peaks around 32 ° and 47° were occurred. This result implies that small amount of α--TCP and β-TCP were existed in the ceramics. The existence of α-TCP and β-TCP are due to gradual loss of the radical OH^- in the structure when HA is heated in air to above 800°C [20]. This process called dehydroxylation which is irreversible process. It has been also suggested that during heating HA tend to lose H_2O at above the critical point.



(a)



(b)

Fig. 8.4 XRD for HA ceramics: (a) conventional sintering method, (b) rate-controlled sintering

Density of samples sintered at various temperatures for the both two methods is shown in Fig. 8.5. The samples prepared by rate-controlled sintering method exhibited a higher density than that of the conventional method. Abrupt change in density was observed in the samples fabricated by the rate-controlled sintering method. The maximum density of the HA ceramics are 3.1 and 2.9 gm/cm^3 for rate-controlled sintering and normal sintering methods, respectively. The optimum sintering temperature to achieve the maximum density is of 1250°C and a slight fall in density with sintering temperature was observed for both methods. The result suggests that the rate-controlled sintering method improve the densification behavior of the HA ceramics compared with the normal method. In the rate-controlled sintering method, we used the fast heating rate of 900°C/h for the first state to by pass the surface diffusion. It was reported that the temperature 850°C is the beginning level of densification with out sintering[46]. In addition, the major densification was occurred at the temperature of 900-1150°C. Therefore in the present work, we held at 850°C and then heat the samples up to1050°C to achieve the major densification for the second state. The slow heating rate of 60°C/h was used in the third state, to slow the densification and to remain open pores as long as possible. At the final state, the slow cooling rate was performed to close pores. Therefore, high density of HA ceramics were obtained after the rate-controlled sintering processes was applied.

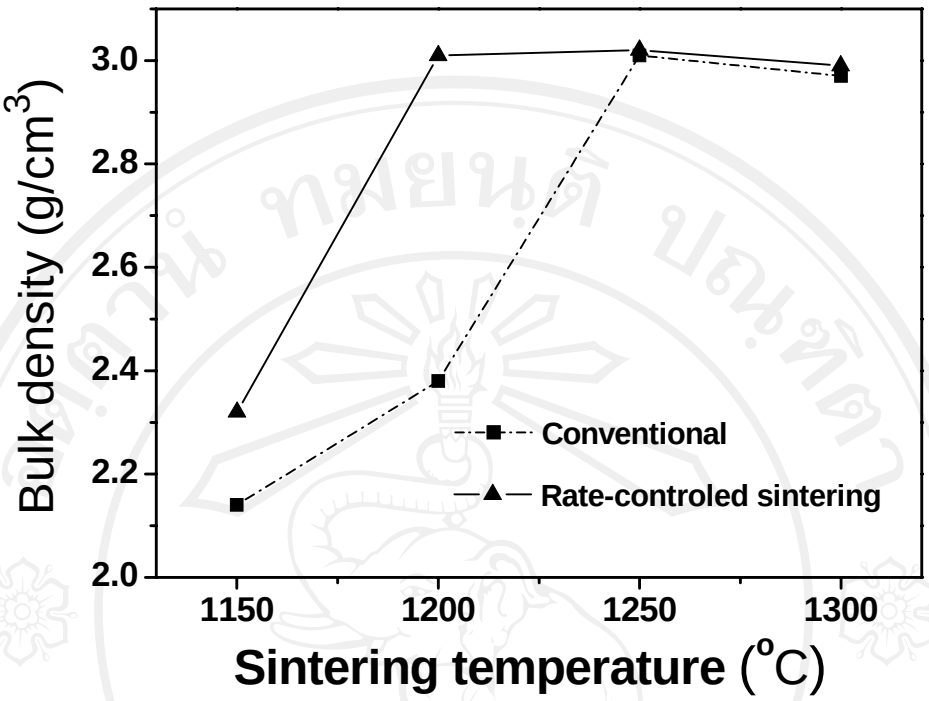
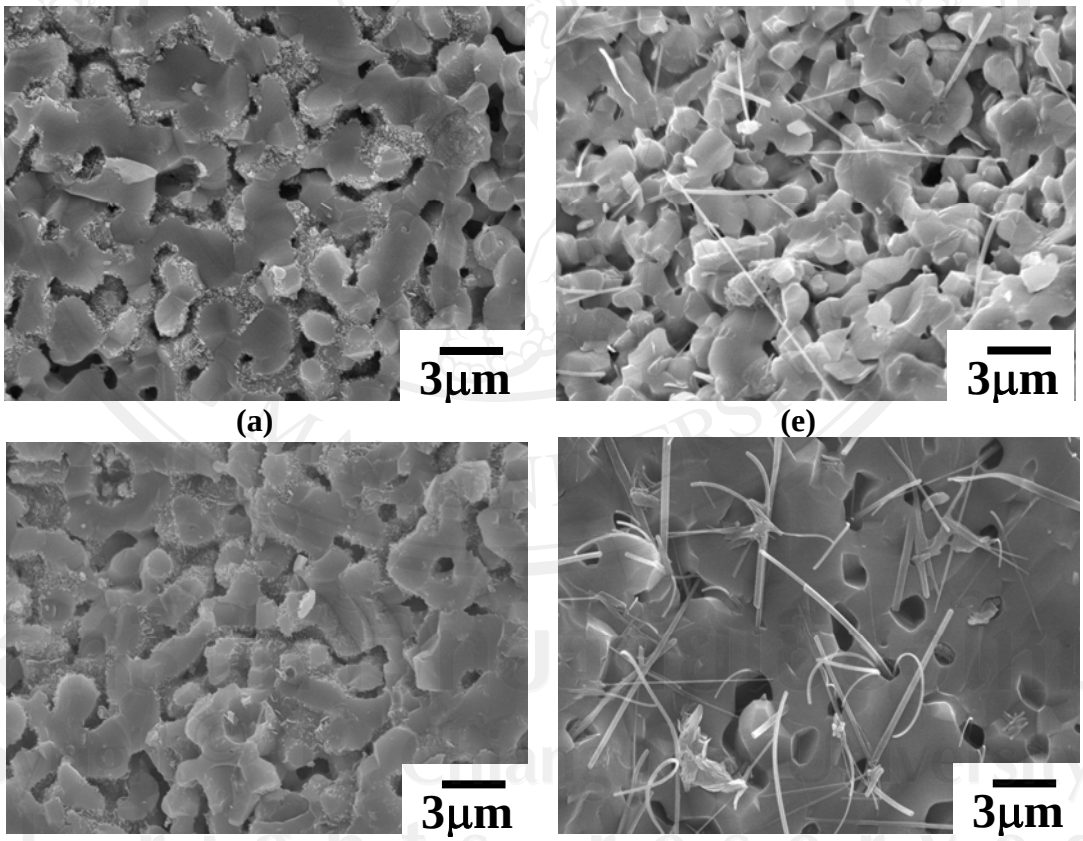


Fig. 8.5 Density of HA ceramics prepared by normal sintering and rate-controlled sintering method.

Fracture surfaces of HA ceramics at various sintering temperature are shown in Fig. 8.6. The fracture surfaces of samples prepared by conventional method indicate a change from predominantly inter-granular fracture to intra-granular (transgranular) cleavage at the sintering temperature of 1250°C. However, change of fracture mode was found at 1200°C for the sample prepared by the rate-controlled sintering method. It can be noted that the SEM evidence can be related to the density result, i.e. abrupt change in density occurred when the fracture mode is changed. In case of rate-controlled sintering method, the fracture mode occurred at 1200°C which is lower than that of the normal method. Therefore, the ceramics prepared by rate-

controlled sintering method shows very rapid densification kinetics. This process is accompanied by the formation of large stable pores and rapid local coarsening of grain structure at high temperature. In addition, nanowire structure was observed at the fracture surface of the samples prepared by rate-controlled sintering method. Fig. 8.7 shows the high magnification SEM micrograph of the nanowire structure which occurred at the fracture surface of HA. It is believe that this nanowires is a glassy phase of the samples which may results from capillary force when the pore was closed at the sintering process.



(a) **(e)**

(b) **(f)**

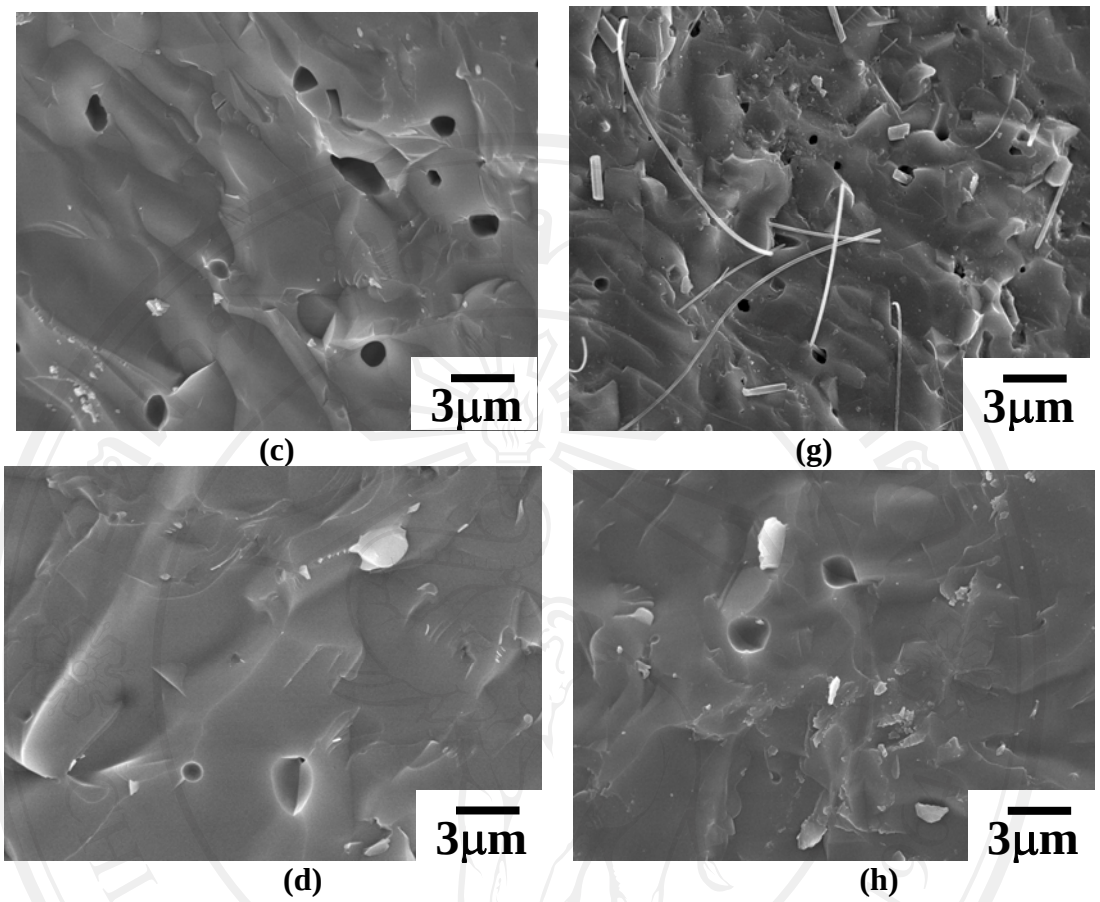


Fig. 8.6 Fracture surfaces of HA ceramics prepared by normal sintering method (a-d) and rate-controlled sintering methods (e-h) sintered at: 1150^{o}C (a and e),1200 ^{o}C (b and f), 1200 ^{o}C (c and g), and 1250 ^{o}C (d and h).

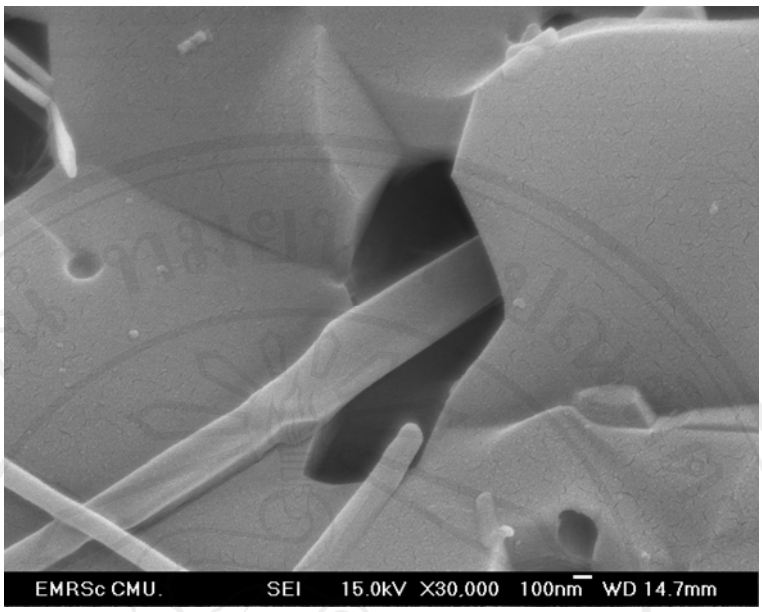


Fig. 8.7 Nanowire structure at the fracture surface of HA ceramics prepared by rate control sintering methods.

The results of hardness measurements are shown in Fig. 8.8. Vickers hardness data indicates that sintering temperature increased the hardness of all samples. The rate-controlled sintering method produced a higher hardness compared to the normal method. For the samples sintered by rate-controlled sintering method, there was a sharp increase hardness from 98 HV for sample sintered at 1150°C to 440 HV for sample sintered at 1250°C, but subsequently there was a more gradual increase reaching 450 HV for the 1300 °C sintered samples. It can be noted that, the increased hardness is in agreement with the change in the observed mode of fracture, from inter- to intra-granular. Therefore, the rate-controlled sintering method has significantly improved the hardness of the sintered samples due to the improvement of density and the change of microstructures.

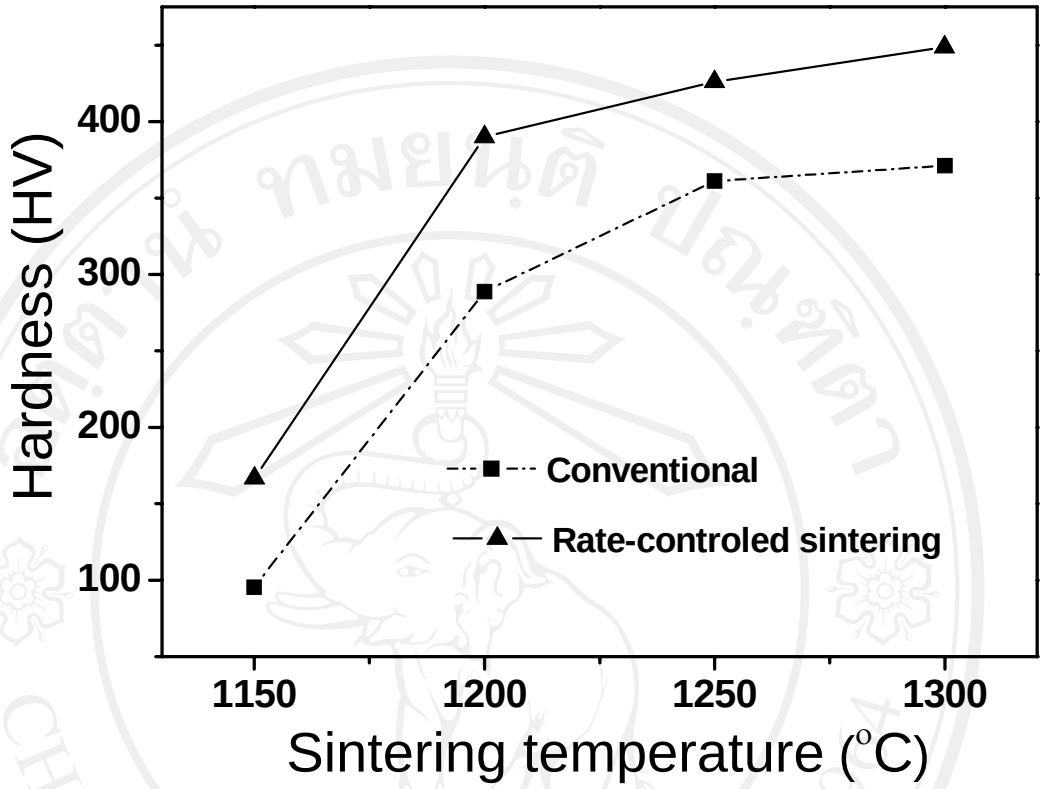


Fig. 8.8 Vickers hardness as a function of sintering temperature of HA ceramics prepared by normal sintering method and rate control sintering methods.

Bending strength as a function sintering temperature for all samples is shown in Fig. 8.9. The result shows that rate-controlled sintering method produced higher strength than that of the normal sintering. In case rate-controlled sintering method a sharp increase in strength was observed at the sintering temperature of 1200°C, but the strength values was found to decrease for the sample sintered at 1250°C. In normal sintering samples, linear increase of the strength was found for samples sintered at temperatures 1100-1250°C; follow by a decreasing at 1300°C. The highest

bending strength of 88.6MPa was observed in the sample sintered by rate-controlled sintering method at temperature of 1200°C, which is a 212% improvement compared to the strength of normal sintering samples. However, the reduction of strength at higher sintering temperature in this work may be due to the formation of glassy phase.

Form Fig. 8.6(f), the rate-controlled sintering sample sintered at 1200°C produced a composites structure between the nanowire and HA ceramics with highly dense structure. The change mode of fracture from inter-granular fracture intra-granular cleavage was also found in this sample, indicating that an increase in grain boundary strengthening. Therefore, the result in the obvious high bending strength of the sample may be due to the fiber reinforce, high density and great grain boundary strengthening. Furthermore, it is reported that the existent of small amount β-TCP can help to improve the mechanical properties in HA ceramics[2,16-19,28]. This small amount of β-TCP may also contributed to the obvious high strength of the ceramics.

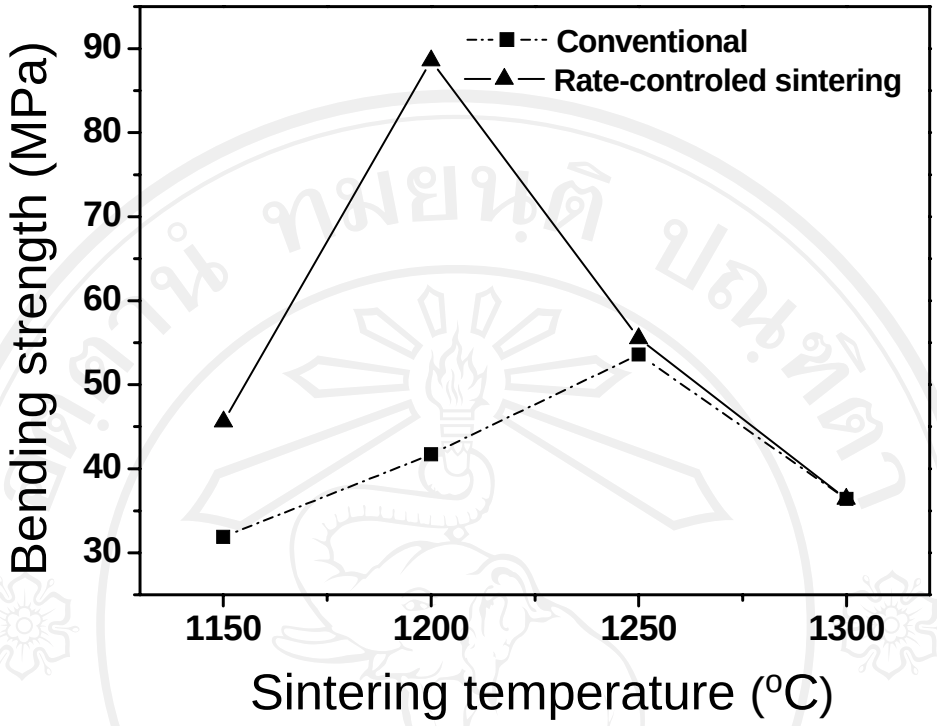


Fig. 8.9 Bending strength as a function of sintering temperature of HA ceramics prepared by normal sintering method and rate control sintering methods.

8.4 Conclusions

In present work, we demonstrated that densification and mechanical properties of HA ceramics which fabricated from HA nanopowder could be improved by the rate-controlled sintering method. The optimum sintering temperature was reduced and the high mechanical properties were observed for samples prepared by the rate-controlled sintering. However, the existence of glassy phase at higher sintering temperature resulted in the lower failure strength.