Effect of Sintering Temperature on Hydroxyapatite Compact Scaffold Characteristics

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***Abstract*— Hydroxyapatite (HA) is a bioceramics with composed of phosphate and apatite that a chemical composition similar to human mineral tissue. It can be synthesized from many natural sources with calcium-based structures, such as bovine bone, mollusk shell, silk cocoon, and coral. Currently, HA is commonly applied in medicine as a dentin bone or bone grafting substitute in orthopaedic surgery, and may be formed into an appropriate scaffold for implantation. Spark Plasma Sintering (SPS) is a new sintering technique, also known as field assisted sintering technique or pulsed electric current sintering, which can produce a dense structure from powder material. This study utilized the SPS process to fabricate the HA compact scaffold as well as investigated the effect of sintering temperature on the scaffold's physical and mechanical properties. The morphology and composition of the specimens were verified by scanning electron microscope (SEM) and X-ray diffraction (XRD). Density and hardness were evaluated using Archimedes's principle and the knoop hardness test, respectively. The results revealed that both density and hardness of the sintered specimen decreased when the sintering temperature increased. The maximum hardness of HA compact scaffold was 3.66 GPa when the sintering temperature was 1,000 ˚C, while the maximum density of scaffold was 3.07 g/cm^3 at 1,050 ˚C.**

Keywords—Hydroxyapatite, Spark plasma sintering, Compact scaffold

I. INTRODUCTION

Bioceramics have been commonly implemented in many biomedical applications due to appropriate properties compatible with human bone structures. Hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is one of the bioceramics which has a characteristic similar to the components of natural bone mineral. It has a calcium to phosphate ratio of 1.67, which is alike that of the natural bone. Therefore, HA is the most appealing material for applied as orthopedic implants and dental replacement [1]. Moreover, HA can be synthesized from a various natural resources, such as mollusk shell, coral, eggshells, human teeth and bovine bone [2-3]. In general, HA needs to be formed into a compact or porous scaffold depending on the conditions of bone substitution before implanting in human body. A variety of forming techniques have been explored to develop compact scaffold of HA, such as compression forming and injection molding techniques. Among many forming techniques, Spark plasma sintering (SPS) is an innovative method that has been employed to fabricate a compact structure because this process can form very dense structure in a short processing time and suitable quality of the formed specimen [4]. Moreover, the restriction of HA at high temperatures during sintering should be examined due to HA decompose to tricalcium phosphate (TCP) and tetracalcium phosphate (TTCP) at 1,300 ˚C in the air or 1,000 ˚C in the vacuum atmosphere [5]. When compared the conventional sintering and SPS technique, the SPS technique makes feasible sintering under heating to high density at relatively lower temperature and shorter sintering duration which would be profitable in restraint exaggerated grain growth [6]. The application of SPS processing techniques can be improved the mechanical properties and bioactivity, but the decomposition of HA at 1,200 °C has been strongly declined the mechanical strength of composites [7].

This study focused on the implementation of SPS for HA compact scaffold fabrication as well as the investigation of process conditions to the characteristics of the compact scaffold. Hardness and density evaluation of the specimen were performed to identify the mechanical and physical properties of the specimens as well as to compare current study with the previous study [8].

II. Materials and Methods

A. Preparation of HA

HA powder in this study was synthesized from natural resources as cortical bovine bones using the preparation steps from the previous study [9]. First of all, the bovine bones were cut into small pieces and soaked in H_2O_2 solution to remove the ligaments and tissues, then boiled in water to eliminate organic substances and collagen. Next, these bones were kept in the hot air oven at 120 °C for 7 hours to reduce their moisture. The dried bones were then calcined at 850 °C for 3 hours [10] with a heating rate of 5 °C min^{-1} [2] before grinding into powder using a high speed ball milling machine. The average particle size of the HA powder is less than 5 μm.

B. Fabrication of compact scaffold

The HA powder was sintered on SPS system (Sumitomo Coal Mining, Japan). Prior to sintering, HA loose powder was filled in a graphite die (15 mm in diameter) and cover with the carbon sheet and punch unit before putting in the SPS chamber. The uniaxial pressure (set at 30 MPa) was applied throughout the sintering process. In order to investigate the effect of sintering temperature on the characteristics of HA scaffold, 5 temperature conditions were varied ranging from 1,000 to 1,200 °C. The sintering temperature was increased within 10 min of heating duration, resulting in a heating rate higher than 100 °C/min., and kept at a desired temperature for 20 min with an applied DC pulse electrical discharge, finally was cooled at the cooling rate of 100 °C/min. Consequently, the whole sintering process was about 40 min. The sintered compact scaffolds were polished and removed the carbon sheet on the surface prior to the characterization step.

C. Characterization of compact scaffold

Characterization of HA specimen was evaluated for phase identification by X-ray diffraction (XRD), which was examined using a RigakuMiniFlex II desktop x-ray diffractometer and CuKα radiation. The data were collected based on 2θ range of 20 - 60° with a scanning rate of 0.02°/step.. Moreover, optical microscope (OM) and scanning electron microscopy (SEM) were employed to examine the surface and cross section morphology of the compact structure. Furthermore, the specimen was tested its hardness and density using Knoop hardness test and Archimedes's principle, respectively.

III. Results and discussions

The HA powder synthesized from bovine bone was successfully formed into a compact scaffold. Fig. 1 shows the diffractogram of the HA compact scaffold sintered at different sintering temperatures. According to the JCPDS-ICDD Card no. 9 – 432 [11], all HA specimens were resembles the naturally occurring bone apatite. Comparing to the initial powder, the intensity of peak corresponding to HA increased with increasing sintering temperature, indicating that increase in crystalinity. In contrast to the previous studies [4, 8], even though the sintering temperature was above 1000 under vacuum condition there was no evidence of HA decomposition. This could be due to a relatively high heating rate employed in this study, more than 100 °C/min although holding time was as long as 20 min. A rapid heating rate could result in a large thermal gradient under SPS process. Moreover, the XRD patterns among these sintering temperature conditions were insignificantly differences in term of the diffraction peaks.

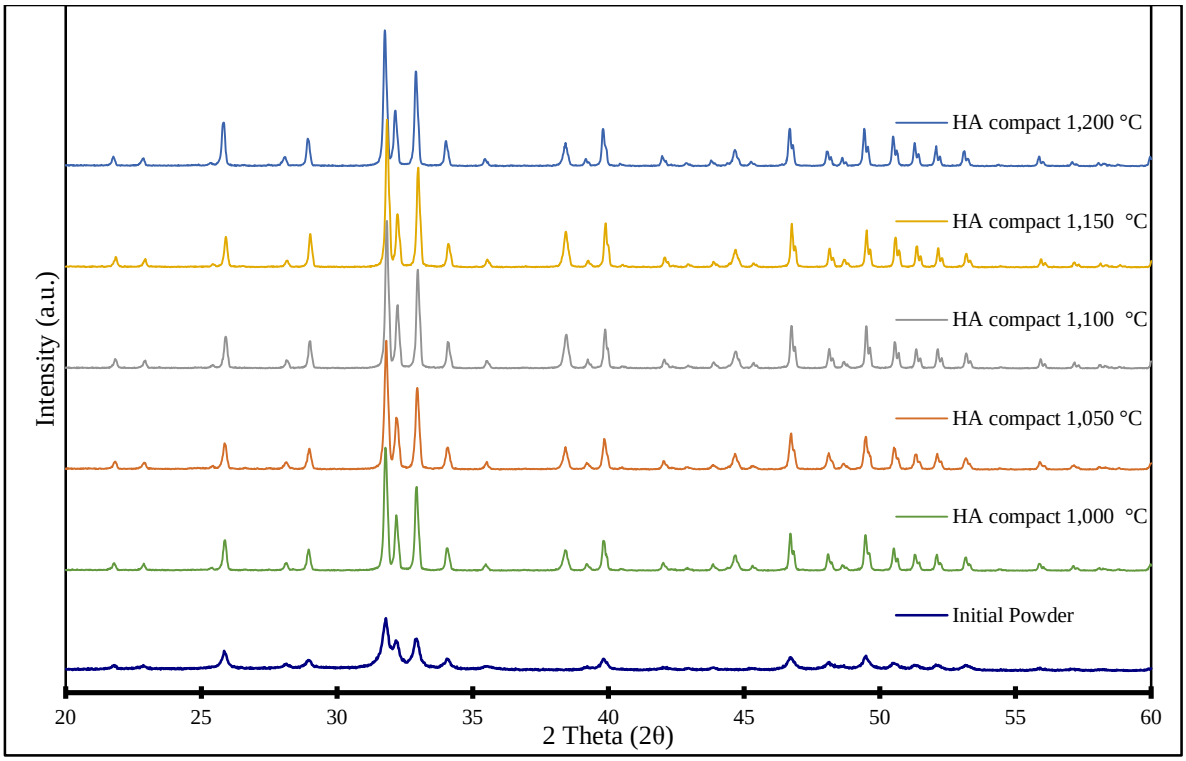

Fig. 1. XRD Pattern of HA Compact Scaffold

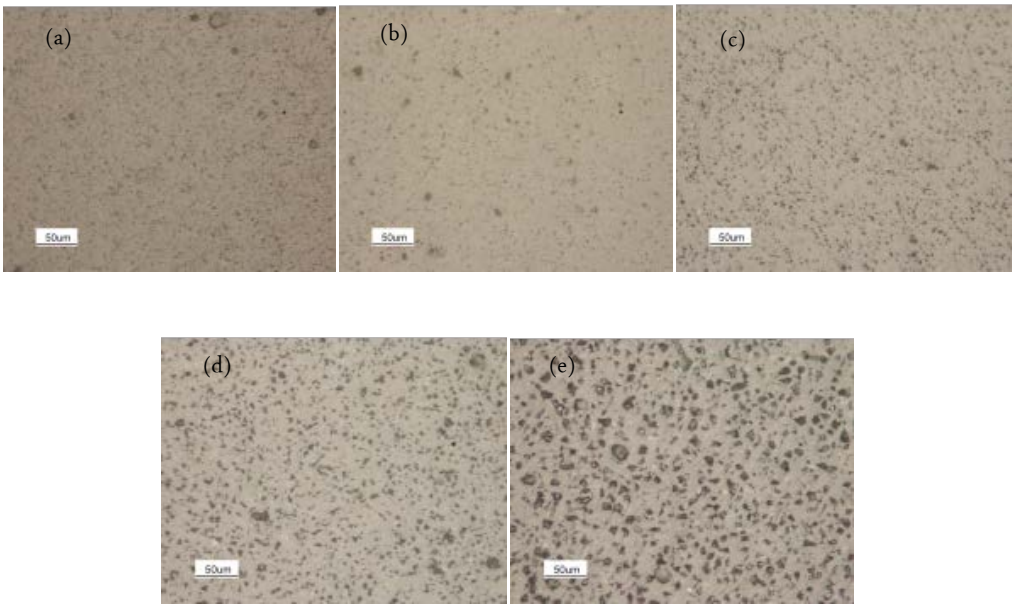

Fig. 2. Optical Microscope Image of HA Compact at Various Sintering Temperature (a) 1,000 °C (b) 1,050 °C (c) 1,100 °C (d) 1,150 °C and (e) 1,200 °C

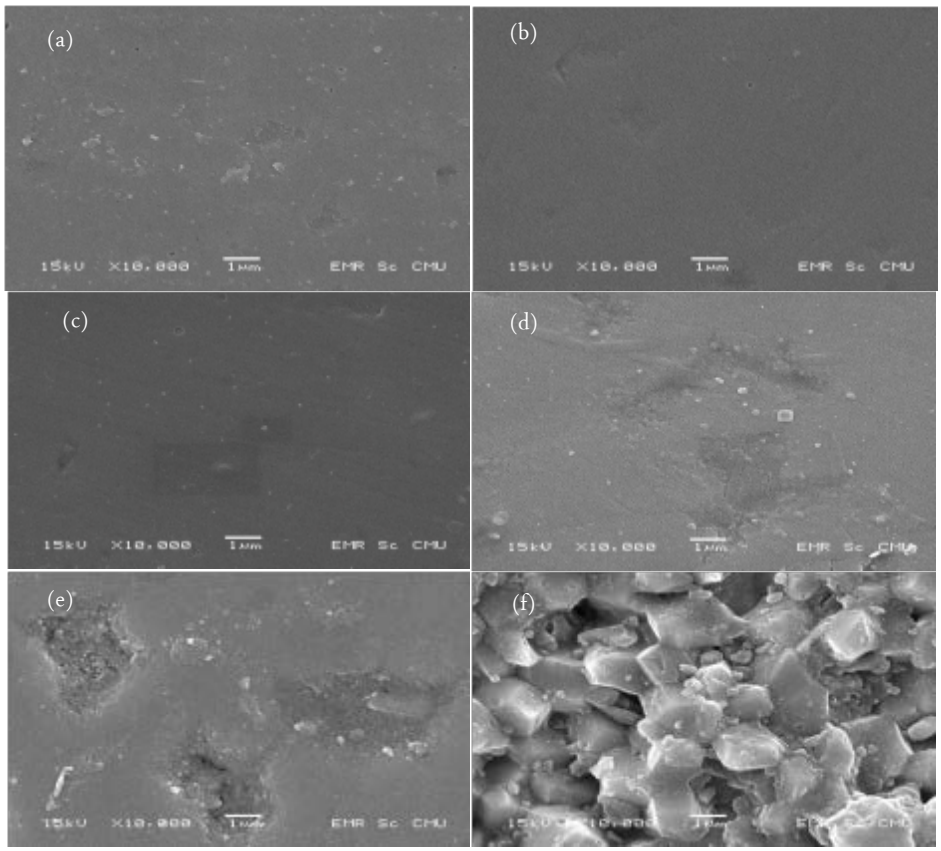

Fig. 3. . SEM of HA compact at various sintering temperature (a) 1,000 °C (b) 1,050 °C (c) 1,100 °C (d) 1,150 °C (e) 1,200 °C and (f) cross-section view of HA compact at 1,050 °C

Fig. 2 shows the images of HA compact scaffold taking from OM. These images reveal surface topography of the specimens at different sintering temperatures. According to these microstructures, it shows that when the sintering temperatures increased, the porosity percentage on the specimen's surface was significantly increased. It can be suggested that the increase in porosity was a result of grain coarsening effect.

When using SEM to explore the topography of these surfaces (as shown in Fig. 3 a-e), it could be seen clearly that the pores on the surface of the sintered specimens were hardly observed in small selective area of specimen at lower sintering temperature. The pore size appeared to be larger as the sintering temperature was increased. Fig. 4 (f) shows the cross section of center compact. It was clearly seen that the morphology at the center was different from the surface. It can be concluded that the grain coarsening was not active at the center of the compact due to a rapid heating.

Fig. 4 illustrates the result from the density test, which showed that the density of the compact scaffold was decreased when the sintering temperature increased. These results showed quite similar behavior as the previous study by Que et al. (2008) [8]. Compared to the previous study, the difference in density at the sintering temperature 1050°C or more could be attributed to grain coarsening at the surface and remaining of porosity at the center of the scaffold.

The hardness of the HA sintered compact scaffolds was illustrated in Fig. 5. As can be seen from this graph, the hardness of HA compacted was fairly consistent when the sintering temperature below 1100°C and significantly decreased at higher temperature. The hardness trend was found to be different with the previous study. The main reason could be the porosity observed at the high sintering temperature.

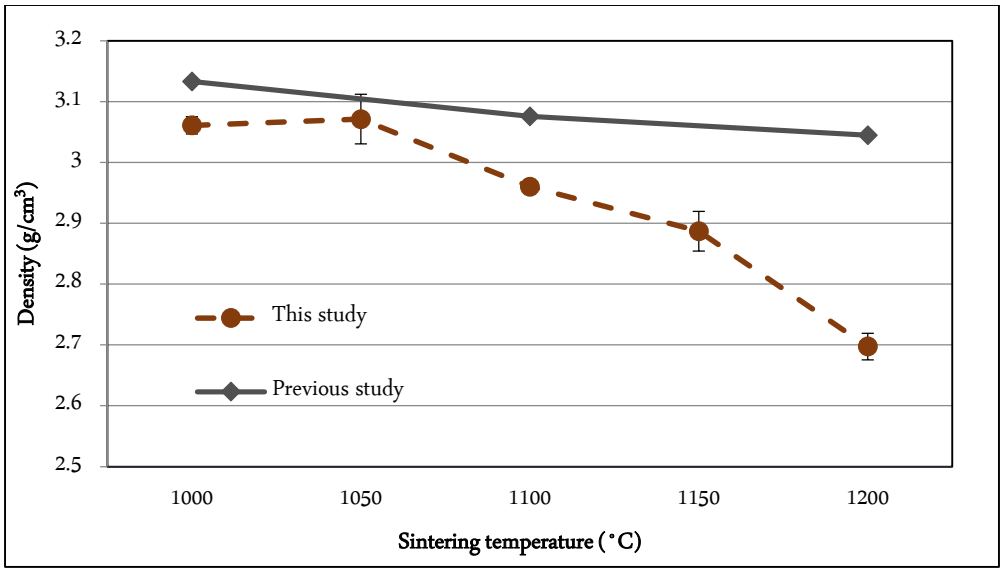

Fig. 4. Comparative Study of Density

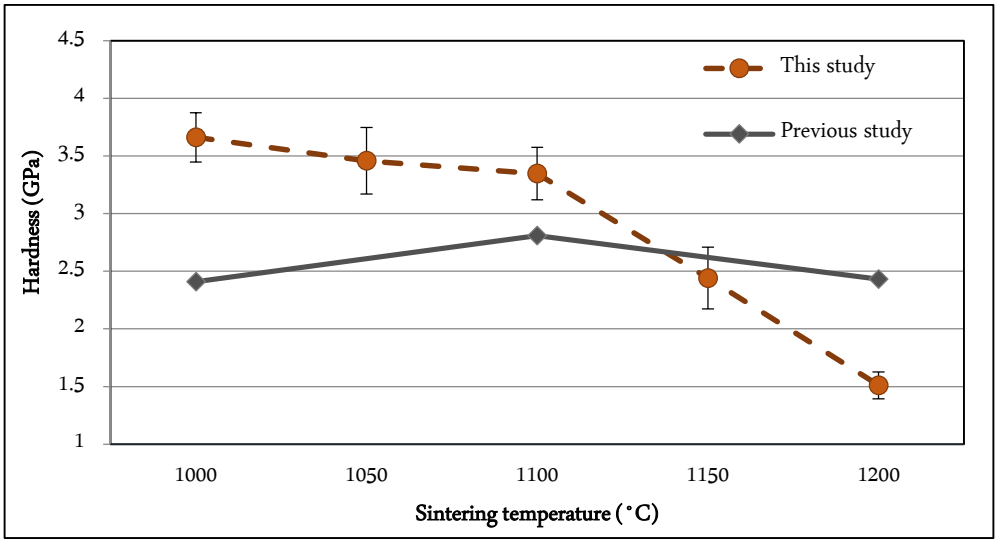

Fig. 5. Comparative Study of Hardness

IV. Conclusion

HA was successfully synthesized using natural based material as a precursor, and it was possible to fabricate HA compact scaffold by using the SPS technique. According to the results, when increasing the sintering temperature, both density and hardness of the compact scaffold were decreased. Possible cause of this reduction could be the formation of pores, which could lessen the density and the hardness of the sintered specimen. With respect to the current investigation, the best characteristics of compact scaffold were 3.66 GPa of hardness at 1,000 ˚C and 3.07 g/cm3 of density at 1,050 ˚C, which were moderately different from the previous study [8], which were 2.81 GPa of hardness at 1,100 ˚C and 3.133 g/cm3 of density at 1,000 ˚C. Future study will focused on other scaffold characteristics such as biocompatibility and osteoconductivity, in order to investigate the potential of product implementation for medical application.

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BIOGRAPHY

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