Microstructure mechanism of the hydroxyapatite densification process

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Abstract. Hydroxyapatite (HA) is a well-known material used as biomaterials in various applications. Numerous studies have been done for unlocking the pros and cons of this material. Sintering process has been used for extraction of pure HA that have similar Ca/P ratio to human bone mineral. This study aims to investigate the effect of sintering temperature on the properties of synthetic HA as well as to develop the mechanism of this densification process. Synthetic HA powder (Sigma-Aldrich #04238) was mixed together with binders, namely polyvinyl alcohol (PVA) and polyethylene glycol (PEG) in wet mixing condition using ball mill. Pressed HA (15 g, 65 mm x 12 mm) was sintered with temperature ranging from 1000°C to 1200°C with heating rate and cooling rate of 10°C/min. It has been found that, pure HA was obtained when the HA was sintered with temperature ranging from 1000°C to 1200°C. The thermogravimetric analysis showed that there are two mass loss stages on the heating process from room temperature to 1250°C; 100-500°C (dehydration) and 680-1080°C (decomposition). From the microstructure data, the mechanism of the densification process of HA was developed.

1. Introduction

Hydroxyapatite (HA) is a bioceramic material which is chemically and mineralologically similar to the non-organic component of natural bone and teeth (highly biocompatible and osteoconductive). It is a well-known material for treating bone defects. Current biomedical applications of bioceramics are commonly carried out in orthopaedic and dental implant coatings, dental implant materials, bone-graft substitute materials, and bone cement [1].

HA has no carcinogenic properties and does not trigger allergic reactions. Nevertheless, despite its advantages, the application of this bioceramic material is limited due to its other less desirable characteristics such as poor resorption, a substantially high Young modulus, and low fracture toughness [2-3].

HA has been studied for biomedical application due to its similarity in terms of chemical and structure with natural bone and teeth [4-5]. HA is also used as biocompatible coating material to improve the bonding quality between metallic substrates and the surrounding bone tissue following implantation [6].
One of the factors that limits the consumption of this material is the brittle property of calcium phosphate group. The beneficial biocompatible properties of HA are well documented in previous studies. It can be integrated into the human body, and at the same time, the body is not wise as to the invasion of a foreign body, although it is only a friendly invasion. However, poor mechanical properties (in particular fatigue properties) mean that this material cannot be used in bulk form for load bearing applications such as orthopaedic [7-9]. It is important to consider the properties, morphology and porosity of HA, especially after the sintering process before considering it to be used as a biomedical material in the medical industry. The HA had a Ca/P ratio 1.67 which is one of the important characteristics of bioactive material as it can provide more sites for bone growth in the human body [10].

There is the existence of countless number of phosphate compounds, as well as highly complex system of calcium phosphate system. This is further complicated by the sensitive stability of phosphates to the minor changes in terms of composition, pH, and reaction conditions (e.g. temperature). It is important to acknowledge the fact that the purity and particle characteristics of the final synthesised powder can affect the bioactivity, mechanical and biological dissolution properties [11]. These characteristics could determine the medical application of the material, which makes it imperative in developing a synthesis method that enables the control of crystal morphology, chemical composition, crystallinity, particle size distribution, and agglomeration.

Thermal stability of HA is an important issue since the implants are usually prepared by high sintering temperature (1000-1350°C) of compacted HA powder. The temperature and time of thermal treatment are the most important parameters that could influence the HAP properties. During the sintering process, there is the occurrence of two separate processes that affect the morphology of solids: densification and grain growth [12]. Two of them are thermally activated, but only densification process is desired. In the first step of sintering process (in temperature below 750°C), the internal powder expansion is observed. Subsequently, the initiation of higher temperature compaction process would lead to the removal of pores from the material. Finally, the sample is shrunk and reached its maximum density in sintered form. Sintering is conducted to achieve the highest density while reducing grain growth [13].

Decomposition of HA at high temperatures is frequently encountered during the fabrication of HA ceramics. This process inhibits the sinterability of the apatite ceramics and completely transforms HA into a mixture of TTCP and TCP, and α-TCP can readily react with water. When the reactions occur in the bioceramics under physiological conditions, the mechanical integrity of HA would deteriorate. The microstructures could correlate well with the density (directly proportional), and the bulk density of HA increases when increasing the sintering temperature [14]. Increasing the sintering temperature beyond 1050°C could resulted in grain growth, and almost full densification was accomplished when compact HA was sintered at >1050°C. The present study deals with the extraction of pure HA via sintering process with different mixing ratio with binders. The mechanism of HA densification process is developed in this study.

2. Materials and Methods

2.1. Preparation of sintered HA
The HA powder (Sigma-Aldrich, #04238) was used to produce a rectangular specimen to study the properties of these materials with varied processing parameters. The rectangular HA specimens were prepared by mixing binders, namely polyvinyl alcohol (PVA) and polyethene glycol 6000 (PEG) in wet mixing condition using ball mill. This process took 24 hours and 160 rpm rotational speed. Then, the slurry was dried in an oven. Next, the slurry was crushed and sieve through a 250 µm mesh. The HA powder was then pressed using uniaxial press machine to shape it into a rectangular (65 mm x 12 mm). After that, the green body of HA specimen undergo a sintering process with temperature ranging from 1000°C to 1200°C. This was accompanied with heating and cooling rate of 10°C/min. The mixing ratio
of the HA specimen are tabulated in Table 1. The sintering temperature was set based on the thermogravimetric analysis for HA, PEG and PVA.

Table 1. HA specimen mixing ratio and its abbreviation.

| Abbreviation | Material (% wt) |
|--------------|----------------|
|              | HA  | PEG | PVA |
| HAP 1        | 100 | 4   | 0   |
| HAP 2        | 100 | 3   | 1   |
| HAP 3        | 100 | 2   | 2   |
| HAP 4        | 100 | 1   | 3   |
| HAP 5        | 100 | 0   | 4   |

2.2. Characterisation and testing
The thermogravimetric analysis (Linseis, Thermobalance Simultaneous Thermal Analysis (STA) TG + DTA, Germany) was used to identify the mass loss of the HA, PEG and PVA. The mineralogical properties of HA were characterised using X-ray diffractometer (XRD, Bruker D8 Advance). The microstructure of failure surface was captured using field emission scanning electron microscopy (FESEM, JSM-7600F, Joel Ltd., Japan).

3. Results and Discussion

3.1. Thermogravimetric analysis (TGA)
The initial weight of HA, PEG and PVA was set at 27.0 mg with heating rate 10°C/min. The TG curve showed that there were two mass loss stages on the heating process from room temperature to 1250°C; 100-500°C and 680-1080°C. At the first stage, removal of adsorbed water from the surfaces and pores of hydroxyapatite took place. Meanwhile, the dehydroxylation of the decomposed HA powder occurred on the second stage at the temperature of 680-1080°C. The total mass loss at Stage 1 and Stage 2 were 5.5 % and 1.2 % respectively. According to previous studies, sintered HA at 1250°C and above (Stage 3 in Figure 1) will lead to the formation of other phases such as alpha tricalcium phosphate (α-TCP) and other resorbable phases of calcium phosphates [15]. These phases had poor mechanical property and higher solubility than pure HA phase. In addition, the amount of HA mass loss increased with the increment of sintering temperature. The results were parallel with previous studies using another commercial HA powder [16].

Moreover, it was expected that hydroxyapatite powder with pure HA phase to be the final product of HA. Therefore, to achieve this stage, the sintering temperature was ranged between 1000-1200°C. At these temperatures, the binder agents burned out and increased the density and mechanical properties of the final product [17]. It was observed that total mass loss (burnt off) for PEG 6000 was occurred at 600°C and above 700°C for PVA. In this study, binders were used to hold the HA compacted particles in the pressing process to form rectangular specimens. Both binders did not give any effect to HA because it burnt off at high sintering temperature (> 700°C).

3.2. Mineralogical
Figure 2(a) indicated that the HA phase was stable during sintering up to 1200°C and there was no presence of TCP (α-TCP or β-TCP). It was observed that long soaking or sintering time did not lead to any changes in phase groups. On top of that, there was no glassy phase formation detected in any specimens, which may cause the material to be brittleness [18].

Furthermore, the XRD diffractions of HAP 3 specimens as a function of sintering temperature are presented in Figure 2(b). The diffractions demonstrated that there were no other phases except HA peaks on the specimens, even when the sintering temperature were varied up to 1200°C. This was in
agreement with previous findings, which was that only HA phases of calcium phosphate groups will be present on the specimen unless higher sintering temperature is applied (> 1250°C). Moreover, other diffractions also demonstrated similar pattern (peak intensity). This showed that sintering temperature in the range of 1000°C to 1200°C did not have much influence on its peak intensities. Since binders (PEG and PVA) were burnt off completely at sintering temperature between 600°C - 700°C, there was no PEG or PVA peaks observed (this was confirmed with the TGA results shown in Section 3.1). The binders provided better compaction during HA sample preparation (pressing process).

The XRD profiles of sintered HA as a function of binder ratio are shown in Figure 6.14 there was no phase decomposition of HA into secondary phases such as α-TCP, β-TCP, TTCP or CaO. Also, the addition of binders (PEG and PVA) onto HA specimen with varied mixing ratios from 1 wt % to 4 wt % did not influence the XRD phase of HA. Moreover, there was no remarkable PEG and PVA peaks observed on the diffractive angle of 23.34°, as marked on the figure where it was supposed to be present [20]. Other than that, all diffractions showed similar patterns, as discussed earlier. All peaks and intensities were also identical.

3.3. Microstructure of failure surface

Figure 3 indicated that the number of open pores were reduced by increasing the sintering temperature, enabling the increase of the HA specimen grain size and eliminate its porosity. In Figure 3(a), numerous small open pores on the cross-section of failure surface of HA at low sintering temperature (1000°C). Then, the number of open pores decreased as the sintering temperature increased. At low temperature, the specimen exhibited many small sizes of open pores. The failure began at pores, passes through the grains and went further into another pores. Unlike at low temperature, high sintering temperature led to the failure beginning at in between two grains, before it moved on to the nearest pores. This was due to the reduction in the number of pores because the increased in grains size [21]. At high temperature, the small pores merged and formed less and bigger pores.

![Figure 1. TG curve of HA powder at 10°C/min heating rate.](image-url)
Figure 2. XRD patterns: (a) sintered HAP 3 as a function of sintering temperature, (b) sintered HA at 1200°C as a function of binder ratio.

Figure 3. FESEM micrograph: (a) sintered HAP 3 as a function of sintering temperature, (b) sintered HA at 1200°C as a function of binder ratio.

The microstructure images of HA specimens at 1200°C as a function of binder mixing ratios are presented in Figure 3(b). There seemed to be no major difference in the properties of HA specimens at the same sintering temperature, except for HAP 2. The FESEM micrographs supported the mechanical properties observed throughout the study, in which the morphology for all HA specimens at same temperature had similar microstructure except for HAP 2. HAP 2 had slightly different microstructure
in term of grain size and numbers of pores that made its mechanical properties different to other specimens. Moreover, although binders gave small effects on the properties of HA specimens, it still influenced the microstructure of the failure surface. This can be seen on the specimen with the highest PVA element (HAP 5), which had many large pores. This was caused by the PVA not providing better compaction during the compression process, leading to the presence of more pores. Consequently, the mechanical strength and density of the specimen will lower.

3.4. Mechanism of HA densification process

The mechanism of HA densification process is developed based on the microstructure analysis done in Section 3.3. Based on the micrographs in Figure 3, it can be found that there are five stages of densification (grain growth) of HA specimen (Figure 4). At room temperature, green body of compacted HA have brittle properties due to highest porosity (coloured with green) and lowest density (density is directly proportional with porosity). As the temperature increasing, the size of grains is increased which cause to contact between grains being oriented, developed and grown. The pores healing happen (size and number of pores reduce) as the temperature increased that lead to excellent mechanical properties.

![Figure 4. Microstructure mechanism of grains growth (densification) and it explanations.](image)

4. Conclusion

There are two stages of grains growth process for HA; Stage 1 (removal of absorbed water) at 100-500°C and Stage 2 (dehydroxylation) at 680-1080°C. The densification process started with elimination of impurities and adsorbed water (hydroxyl groups) from the surface and pores. As the sintering temperature increasing, the dehydroxylation take place and this process leads to reduction of size and number of pores until it totally removes from the HA at Stage 2 of HA densification process. Reducing in number of pores (porosity) enables the HA gain better mechanical properties (overcome the brittleness of HA) and this widen the application of HA from non-load bearing application to load bearing application. In addition, the size and boundaries of grain increased with increment of temperature and this provides better mechanical properties in term of strength and many more. There are five microstructure mechanism of grains growth for HA developed in this study based on the data from the FESEM analysis.

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**References**

[1] Borkowska A and Ginalska G 2010. Hydroxyapatite Biomaterials for a Filling of Bone Defects. *Annales Universitatis Mariae Curie-Skłodowska* 23 45-52

[2] Mohd Pu’ad N A S, Koshy P, Abdullah H Z, Idris M I and Lee T C 2019. Syntheses of
hydroxyapatite from natural sources. *Heliyon* **5** e01588

[3] Best S M, Porter A E, Thian A E and Huang J 2008. Bioceramics: Past, Present and for the Future. *Journal of the European Ceramic Society* **28** 1319-1327

[4] Kanasan N, Adzila S, Mustaffa N A, Rahman M N A, Hassan M F, and Panerselvan G 2018. Effect of sintering on hydroxyapatite/sodium alginate properties. *International Journal of Integrated Engineering* **10** 78-82

[5] Fara A N K A and Abdullah H Z 2016. Influence of calcination temperature on the microstructure and crystallographic properties of hydroxyapatite from black tilapia fish scale. *International Journal of Integrated Engineering* **10** 78-82

[6] Cahaningrum S E, Herdyastuty N, Devina B and Supangat D 2017. Synthesis and characterization of hydroxyapatite powder by wet precipitation method. *IOP Conf. Series: Materials Science and Engineering* **299** 012039

[7] Cox S 2012. Synthesis Method of Hydroxyapatite. *Ceramics* **2** 1-10

[8] Gu Y W, Loh N H, Khor K A, Tor S B and Cheng P 2002. Spark Plasma Sintering of Hydroxyapatite Powders. *Biomaterials* **23** 37-43

[9] Champion E 2013. Sintering of Calcium Phosphate Bioceramic. *Acta Biomaterials* **9** 5855-5875

[10] Nordin P, Rajendran S, Rajagopalan S, Sopian K and Oktar F N 2009. Effect of Sintering Temperature on Mechanical Properties and Microstructure of Sheep-Bone Derived Hydroxyapatite (SHA). *IFMBE Proceedings* **23** 1271-1274

[11] Monmaturapoj N and Yatongchai C 2010. Effect of Sintering on Microstructure and Properties of Hydroxyapatite Produced by Different Synthesizing Methods. *Journal of Metals, Materials and Minerals* **20** 53-61

[12] Ahmad M, Tay M Y, Shafei M, Hussein M Z and Lim J J 2011. Green Synthesis and Characterization of Silver/Chitosan/Polyethylene Glycol Nanocomposites without any Reducing Agent. *International Journal of Molecular Sciences* **12** 4872-4884

[13] Abdullah H Z 2002. Kesat Zink Oksida (ZnO) Ke Atas Sifat Seramik Hidroksiapatit. Master Thesis. Universiti Sains Malaysia