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Synthesis and Sintering of Nano-crystalline Ca-hydroxyapatite.

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Abstract

The chemical co-precipitation method has been used for the synthesis of nanocrystalline hydroxyapatite (HAP) powder from $Ca(NO_3)_2.4H_20$ and $(NH_4)H_2PO_4$. The thermal stability of the HAP powder was determined. The phase composition of raw-HAP and calcined product were characterized by XRD. The HAP powder has been sintered into micro-porous ceramic in air at different temperature with different time. Sintering kinetics was investigated by determining bulk density and shrinkage of sintered disc. The microstructure of the resulting HAP was characterized by scanning electron microscope. It may be concluded that Ca/P ratio of HAP is dependant on the pH of the precipitation reaction. Ca-deficient HAP is stable upto 900^oC and densification of nanocrystallite HAP is dependant on the time of firing, i.e. decomposition reaction of the HAP.

Keywords: ceramics; hydroxyapatite; nanocrystalline; chemical synthesis;

1. INTRODUCTION

Synthetic hydroxyapatite (HAP) has been used extensively in different medical applications as biomaterials, due to its excellent biocompatibility with human tissues [1-4]. Porous HAP ceramic is only used as cancellous bone graft substitute materials in non-load bearing situations [5]. Where as, dense HAP ceramic has more excellent mechanical performance than porous ceramic [6], but its bone in growth property is not better than the porous ceramic. Pore size and porosity controls are very important, both in terms of the effect on mechanical properties and as a mechanism for enhancing bonding to the bone tissue. The mechanical properties of HAP ceramics can be improved by controlling particle size and shape, particle distribution and agglomeration [7] etc of powder precursors. Nanocrystalline HAP powders exhibit greater surface area [8]. It can provide improve sinterability and enhanced densification to reduce sintering temperature, which could improve the fracture toughness of the HAP ceramic [9]. Moreover, nanometer sized HAP is also expected to have better bioactivity than coarser crystals [10]. So for orthopedic/dental implant formulations with improved osseointegrative properties, nanocrystalline HAP powders are desired and expected to be sintered into nanophase HAP ceramic with better mechanical. In the present investigation, nanocrystalline HAP powder has been synthesized through co-precipitation method. High temperature phase stability and sinterability of the nanosize-HAP powder has been investigated.

2. EXPERIMENTAL

Calcium hydroxyapatite was prepared by mixing stoichiometric amounts of aqueous solutions of $Ca(NO_3)_2.4H_20$ (Nice Chem., Chennai, >99%) and $(NH_4)H_2PO_4$ (Qualigens Chem, > 99%). The solution was heated at 80°C under stirring condition and then the pH of the solution was adjusted to a value of 8 by the addition of ammonia solution. The resultant mixture was aged for 24 hours. The precipitate was filtered and washed with water and IPA. Washed HAP was dried in oven at 40°C. Dried powder was ground properly using pestle and mortar. To check the stability of HAP-phase, the powder was calcined at different temperatures in the range 700°C to 1100°C. For sinterability experiment, the powder was uniaxially compressed at 5 tones into disc shaped sample. The discs were sintered at different temperatures from 700° to 1200°C at 100° interval with different times. Phases of raw and calcined powders were identified by XRD (Phillips PW-1830, CuKα radiation with Ni-filter). Sintered density and apparent porosity was determined by Archimedes's principle. The micro-structure was observed by Scanning Electron Microscope (SEM, JEOL 5200, Japan).

3. RESULTS AND DISCUSSION

It is known that the density of sintered HAP is significantly influenced by the sintering temperature. Generally density of it increases with sintering temperature. Other hand HAP is stable up to a certain temperature and that depends on the stoichiometry i.e. Ca/P ratio of it. In general stoichiometric HAP with Ca/P=1.67 is thermally stable upto temperature near 1300ºC and that with Ca/P ratio less then 1.67 are stable upto only 800ºC [11]. So before sintering experiment it is very much important to indentify the Ca/P ratio of HAP. Fig.1. shows the X-ray diffraction patterns of raw and calcined powders of HAP. The HAP in the raw powder was indexed to match with PDF No. 46-0905, that is with $Ca_9(PO_4)_6H_2O$ and having Ca/P ratio 1.5. So a Ca-deficient HAP was produced in the present case; as the pH of the precipitating solution was about 8, rather than 10 required for stoichiometric precipitation. The pattern also shows that the raw powder contain some amount of hydrated calcium phosphate ($CaHPO_4$). When calcined, that Ca-deficient HAP is transformed to some extent into stoichiometric HAP by reacting with hydrated calcium phosphate that present in the raw powder. At 900ºC it started decomposing into β-TCP and stoichiometric HAP. At 1100ºC it is almost convert to β-TCP. So depending upon the phase requirement, the sintering temperature can be selected. It is also interesting to note that the crystallite size of raw powder (70-80 nm) decreases to 46 nm when calcined at 900ºC. This unusual decrease in crystallite size with calcination temperature was also observed previously [12]. This phenomenon may be due to the re-arrangement of crystallites of Ca-deficient amorphous HAP to form an intermediate structure in the route to stoichiometric HAP formation.

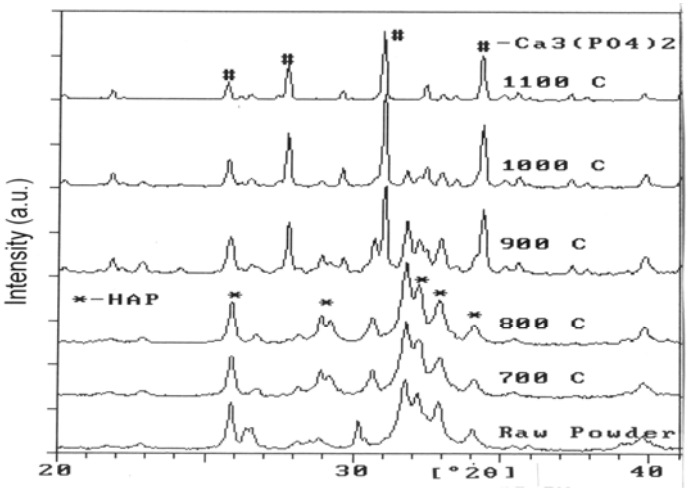

Figure 1. XRD patterns of raw-HAP powder and that calcined at different temperature.

Lattice parameters of the raw HAP and those in different calcined product were calculated from XRD data. Raw-HAP has c_o= 9.4297Å and a_o=6.8815 Å, with c/a ratio of 0.7297, which is very similar to the standard phase (c/a=0.7288). The change in c/a ratio of HAP with calcination temperature is shown in Fig. 2. It is well known that a-axis decreases and c-axis increases i.e., c/a ratio increases during decomposition reaction of HAP [13]. That ratio increases after 800°C (Fig.2) with calcination temperature due to the dehydroxylation and transformation reaction of HAP.

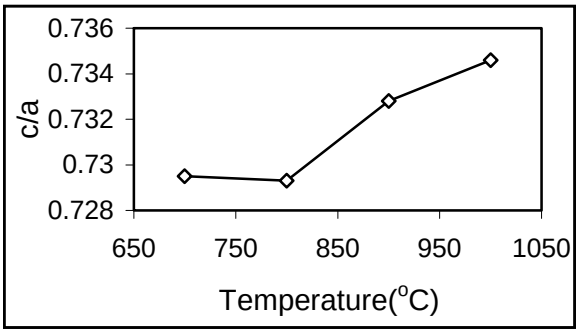

Figure 2. Variation of c/a ratio of HAP with calcination temperature.

The green density of pressed pallets was about 1.97gm/cc. The change in bulk density and apparent porosity of sintered-HAP as a function of dynamic sintering temperature is shown in Fig.3. The dynamic sintering is sintering at the rate 10°C/minute without soaking. Bulk density upto 900°C apparently shows lower value than green density. That may be co-related to the decrease in crystallite size due to dehydroxylation and transformation of phases in the system at that range. After 900°C, BD increases as per expectation with dynamic sintering temperature. Maximum sintered density achieved is 3.022gm/cc. Similarly apparent porosity also decreases with dynamic sintering temperature. As it is mentioned earlier that HAP decomposes into phosphate with the increase in temperature, it can not be fully sintered with normal sintering in air. The transformation of HAP to phosphate affected the values of porosity.

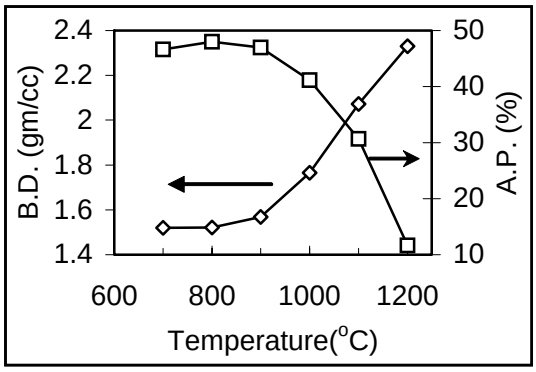

Figure 3. Change in bulk density and apparent porosity of HAP ceramics with sintering temperature.

Sintering kinetics clearly shows (Fig.4.) that bulk density increases with time for a small time period (upto about 60 min.) and then decreases. Upto 60 minutes, the rate of sintering was comparatively higher than the rate of decomposition. After 60 minutes, the rate of decomposition is higher than sintering upto about 240 minutes and the decrease in BD is due to the formation of low density tricalcium phosphate from high

density HAP. Sintered HAP samples shows to contain a sufficient quantity of apparent porosity. The apatites are used as porous ceramics and it is not desirable to get a pore-free body, because, porous body is required for cellular and osteold growth for biomaterials. So, our study can be used to predict the apparent porosity formation in different sintering conditions.

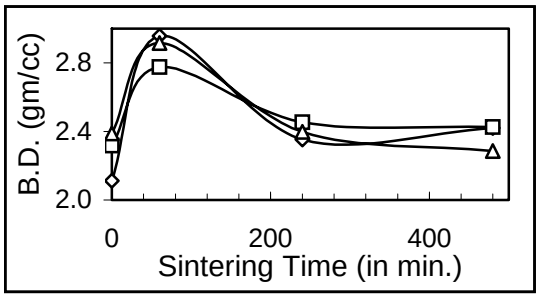

Figure 4. Sintering kinetics of Calcium hydroxyapatite.

Fig. 5. shows the surface microstructures of HAP sintered at 1000°C. The micrograph shows many micro pores having irregular in shape. The pore size was between 3-5 micron, which probably was caused by decomposition of hydroxyapatite, and deficient sintering. Open porosity of that sample was ~31%, which is representative of the microstructure. After sintering calcium hydroxyapatite at 1000°C, grain size is about 1-2 micron that is many times higher than the grain size of the raw hydroxyapatite powder.

4. CONCLUSIONS

Phase pure and nanocrystalline calcium hydroxyapatites has been synthesized by simple Co-precipitation route. The crystallite size of the HAP powder is 70-80 nm. The HAP powder is stable up to 900°C due to its Ca-deficiency nature. The material has been fabricated and sintered with a specific porous structure. Sintering kinetics largely depends on the time of firing. So, it can be used safely up to 900°C.

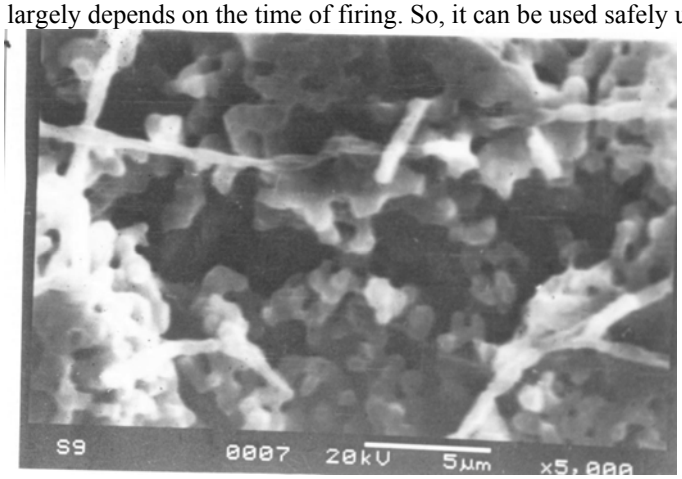

Figure 5. SEM microstructure of HAP sintered at 1000°C.

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