Preparation and Characterization of Hydroxyapatite /Calcium Phosphate Powders

D. Şimşek, R. Çiftçioğlu, Ş. Harsa, M. Çiftçioğlu

Materials Science and Engineering Program,
İzmir Institute of Technology, Gülbahçe, Urla, İzmir

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Abstract. The preparation of calcium phosphate based powders through chemical precipitation in order to determine the optimum conditions for the preparation of stoichiometric, thermally stable hydroxyapatite (HA) powders was investigated in this work. The effects of parameters like pH, aging time, and heat treatment temperature on the phase structure and morphology of the powders were investigated by SEM and XRD. HA was prepared at a Ca/P ratio of 1.67. The precipitation pH had a profound influence on the morphology and crystallite size of the powders in the 4-11 pH range. Relatively large 5µm prismatic particles were obtained at low pH whereas the powders were formed from agglomerates of nano sized particles at high pH. Powders had a HA dominant phase structure above a pH of 8. Phase pure HA powders were obtained with close to theoretical yields at pH = 10 and 11. The crystallite sizes of the powders varied from about 30 nm at 90°C to 50-90 nm at 1250°C with the smallest crystallite sizes obtained for pH 10 and 11 powders at 1250°C. The crystallite size increased significantly with aging temperature.

Introduction

The average 70 kg man contains about 780 g P, of which about 700 g is present as bone apatite corresponding to about 3.5-4 kg hydroxyapatite [1]. Since hydroxyapatite is the main inorganic component of the hard tissues, among all materials it seems to be the most promising material for renewing and regeneration operations because of its excellent biocompatibility.

Synthetic HA powder with composition $\text{Ca}_{(10-x)}(\text{HPO}_4)_x(\text{PO}_4)_{(6-x)}(\text{OH})_{(2-x)}$ $0 \leq x \leq 1$ is commonly prepared by various precipitation techniques. The powder properties may be directly affected by various precipitation parameters like Ca/P ratio of the starting reagents, pH, aging time and temperature, stirring, addition rate of the reactants, etc [2,3,4,5]. The preparation of HA ceramics with a fine microstructure and improved mechanical properties necessitates consolidation of nonagglomerated nano-sized particles and uniform particle size distributions. In this study the effect of pH, aging time and temperature on the powder properties like crystallite size, phase purity, morphology and thermal stability was investigated.

Experimental

Powders were precipitated by the drop wise (10 ml/min) addition of 0,334 M 500cc $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma) solution to 0,2 M 500cc $(\text{NH}_4)_2\text{HPO}_4$ (Merck) solution. pH of the solution was adjusted by addition of NH_4OH at specific pH value at 60°C while stirring. The Ca/P ratio was set at 1,667 in the final reaction medium. The precipitates was filtered and washed several times with deionised water and were further washed with ethyl alcohol to remove the excess water from the precipitate to control agglomerate strength. The precipitate oven dried at 90°C. Six different powders in the range of 4-11 were prepared by aging at 60°C for 24 hrs. The precipitate was aged at 30°C, 60°C, 90°C before filtration in order to understand the effects of aging temperature on powder properties. The aging time was varied in the 0-48 hrs for aging

experiments. The oven dried powders were heat treated in the 300°C-1250°C range by using programmable Carbolite RHF1600 high temperature furnace for the investigation of thermal behaviour of the powders. Phase purity and the structure of the powders were characterized by using Philips X'PERT PRO XRD. The morphology and the size of the powders were further characterized by Philips XL30S SFEG SEM.

Results and Discussion

The complete incorporation of Ca ions in the powder was observed from the amount of precipitated dried powder at pH10-11 based on stoichiometric HA. Only about 65% incorporation of Ca ions was determined at pH4-6. XRD patterns of the oven dried powders at different pH levels is given in Figure 1. At pH 4 the powder is almost phase pure Brushite with a low level of Monetite impurity. Whereas at pH 6 the powder is phase pure monetite both powders are very crystalline. These powders are formed from about 5µm prismatic particles as shown in the SEM micrographs given in Figure 2. The dominant phase at pH 8 and above is HA in the dried powders as shown in Figure 1. The powder morphology is whiskerlike and drastically different with particles in the nano meter scale at and above pH8 as shown in Figure 3a.

Figure 1. XRD patterns of the powders precipitated at different pH values.

This pronounced change in the morphology of the particles forming the HA powders may be explained by the differences in the solubility and the precipitation kinetics as pH increases above 8. The presence of high nucleation rates during precipitation causes the formation of nano scale particles in the powder. There was no significant difference in the crystallite sizes estimated by Sherer equation from XRD pattern using the single peak at 25.8 2-theta degree for the powders precipitated at pH: 8-11 range as shown in Figure 4a. However, after heat treatment at different temperatures up to 1250°C there was an increase in crystallite sizes from ~30nm to 40-90 nm range. But precipitate obtained at pH 8 deviate from this tendency after 900°C. This may be explained by the decomposition of HA into other phases because of initial nonstoichiometry and or crystal imperfections.

Figure 2. SEM micrograph of the precipitated powders at a) pH 4, b) pH 6

Figure 3. SEM micrograph of the precipitated powders at a) pH 10 60 °C 24 hrs, b) pH 10 90°C 24 hrs

Figure 4. Change in the crystal size of the powders precipitated at different pH (a) and aging temperature at pH 10 (b) with respect to temperature.

Two identical precipitates were produced at pH10 and were aged at 30 and 90°C for 24 hrs. Both powders displayed characteristic HA peaks after oven drying. Increasing aging temperature increases the rate of dissolution-recrystallization processes. The powder aged at 90°C had larger crystallite sizes as shown in Figure 4b. Morphology of the powder transforms from nearly spherical to a more elongated structure. Heat treatment results indicated that aging at 90°C leads to the formation of a more stable HA phase at 1250°C.

Another important control parameter for the precipitation of HA is aging time. Four identical precipitates were produced at pH 10 and at 60°C for 0, 1/2, 1 and, 48 hrs aging. The crystallite size didn't change significantly with aging time. The heat treatment temperature was the dominant parameter in the determination of the crystallite size. The XRD patterns of the 1250 °C heat treated powders in the 4-11 pH range is given Figure 5. The pH 4 and 6 powders do have a multiphase structure formed from Brushite Monetite and Alfa-TCP phases. The structure is HA dominant above pH 8 with a minor amount of alfa-TCP. The alfa-TCP peak is the sharpest for

the powder prepared at pH 8. The HA peaks are sharp indicating larger particle sizes in the 1250°C heat treated powders when compared with those in Figure 1.

Figure 5. XRD patterns of the powders, precipitated at different pH values after heat treatment at 1250 °C

Summary

Stoichiometry, crystallinity and the thermal stability of the calcium-phosphate powders can be controlled by changing the precipitation conditions. The results show that in acidic mediums monetite and brushite are dominant phases whereas HA powders can be prepared above pH 8. and powders with thermally stable HA phase was obtained over pH 10. Powders with average crystallite sizes in the 20-40 nm range were prepared by adjusting the precipitation conditions. Consolidation of these powders may yield ceramics with fine microstructures and improved mechanical properties.

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