Selective Laser Sintering of Calcium Phosphate Powders

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Abstract

Various forms of calcium phosphate compounds are prepared from hydroxyapatite($Ca_5(OH)(PO_4)_3$) by reacting with phosphoric acid (H_3PO_4) to prepare powders with Ca/P ratio from 1 to 0.5 for the Selective Laser Sintering (SLS) process. These powders are SLS processed using polymer as an intermediate binder. The produced green parts are infiltrated with the calcium phosphate solution and fired to burn out the binder. In this paper, the characterization of the produced parts are examined as consequences of various Ca/P ratio, SLS operating parameters, and post-processing conditions.

Introduction

Since DeJong first observed the similarity between powder X - ray diffraction pattern of the *in vivo* mineral and the hydroxyapatite ($Ca_5(OH)(PO_4)_3$,HA) in 1926, the calcium phosphate ceramics have received attention as a bone substitute material.

Five calcium phosphates which exhibit different X-ray diffraction patterns are known to be precipitated from aqueous solution at normal pressure. [1] These are $Ca(H_2PO_4)_2$, $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4$, $CaHPO_4 \cdot 2H_2O$, and crystalline precipitate of variable composition of hydroxyapatite with the base formula $Ca_5(OH)(PO_4)_3$. Various forms of calcium phosphate compounds, Ca/P ratio range from 0.5 to 1, are prepared from HA by reacting with phosphoric acid . Thermally dehydrated calcium phosphates are known to form a CaO and P_2O_5 binary system. It is known that for the CaO and P_2O_5 binary system, the chain phosphates appear between the orthophosphate (mole ratio of $CaO/P_2O_5 = 3$) and metaphosphate (mole ratio of $CaO/P_2O_5 = 1$) and ultraphosphate for which mole ratio of CaO/P_2O_5 less than 1. Particularly in the case of metaphosphate, very high degree of polymerization and as a consequence, good mechanical properties are reported. In this binary system, mole ratio of CaO/P_2O_5 less than 55/45 forms a glass-like structure from the melt, and its mechanical properties are known to be nearly same as those of natural teeth.[2]

Materials and Methods

HA was obtained from Monsanto Inc. as Tricalcium phosphate and phosphoric acid was purchased from Fischer Scientific in 85 % concentration. As an intermediate polymeric binder, emulsion poly(methyl methacrylate-co-n-butyl methacrylate) copolymer with a Melt Index of 30.9 g/10min. at 75 psig and 200°C was used.[3]

The mercury porosimeter, Poresizer 9320 from Micromeretics was used to determine the surface area of the powder. The powder samples were heated to expel the absorbed moisture and then stored in desiccator until analyzed. The sample in penetrometer was initially evacuated to 25 *m*Hg. Mercury was then admitted and pressure was increased up to 30,000 psi which is capable of measuring pore size of 0.006 *m*m. Contact angle of 130° was used.

The particle size distributions of powders are measured by a Coulter Multisizer.

1. Powder preparation

(1) calcium metaphosphate ($\{Ca(PO_3)_2\}_n$, CMP)

251 g of HA was reacted with 403g of 85 % phosphoric acid, diluted with 150 g of water according to the following equation.

$$Ca_5(OH)(PO_4)_3 + 7H_3PO_4 \xrightarrow{\text{room Temp}} Ca(H_2PO_4)_2 \bullet H_2O$$

The prepared paste was dried at the room temperature and then heated at 150 °C to drive out the moisture.

$$Ca(H_2PO_4)_2 \bullet H_2O \xrightarrow{150 - 200\ ^\circ C} Ca(H_2PO_4)_2 + H_2O$$

The above equations are not quite exact because of the difficulty in writing a simple formula $Ca_5(OH)(PO_4)_3$ for the HA compositions which does not take into account the variable composition or the amount of hydration. However, the reaction product was confirmed by the X-ray diffraction analysis. Powder that is heated at 150 °C exhibits the X-ray diffraction pattern of mixture of $Ca(H_2PO_4)_2$ and $Ca(H_2PO_4)_2 \bullet H_2O$. This powder is further dehydrated by heating to 900 °C in a porcelain crucible to form stable β -calcium metaphosphate (CMP) which is theoretically composed of 28 wt % of CaO and 72 % of P_2O_5 and reported to have average chain length of 10,000.[4] The X-ray diffraction pattern of CMP made by described method is compared to the standard pattern in Figure 1.

$$Ca(H_2PO_4)_2 \xrightarrow{600 - 700^\circ C} Ca(PO_3)_2 + 2H_2O$$

This thermally coalesced compound is ground by a Szegvary attritor system, type 1HSA to be mixed with polymer for SLS processing.

(2) Calcium pyrophosphate ($Ca_2P_2O_7$, CPP)

CPP was prepared from the 251 g of HA reacted with 196 g of 85 % phosphoric acid by the same way described in the CMP preparation.

$$Ca_5(OH)(PO_4)_3 + 2H_3PO_4 \xrightarrow{150 - 200\ ^\circ C} CaHPO_4\ 2H_2O + H_2O$$

$$2CaHPO_4 \bullet 2H_2O \xrightarrow{700 - 750\ ^\circ C} Ca_2P_2O_7 + 5H_2O$$

(3) Calcium phosphate with 35 wt % of CaO(35CaP)

251 g of HA was reacted with 251 g of 85 % phosphoric acid. X-ray diffraction pattern of this powder, as shown in Figure 1, was identified by JADE X-ray peak identifying program as mixture of major phase of $4CaO3P_2O_5$ and minor phase of CPP.

(4) CPP with 1 wt.% of NaO (1NaCPP)

The prepared CPP powder was mixed with 1 weight percent of NaO to depress the melting temperature in order to study the influence of surface area of the powder on green strength. 1NaCPP was thermally coalesced at 1020°C and then ground in the attritor. The ball milling time was controlled to have different particle size and consequently surface area. Three samples of pore surface area, 1.8 , 1.4, and 1.1 m^2/g, were measured by mercury porosimeter.

2. SLS Processing

CMP powder is mixed with 15 wt.%(30 vol.%) polymer and SLS processed with the following conditions.

Table 1. SLS parameters

Power (W)	Scan Space (mil)	BeamSpeed (ips)	Layer thickness	Bed Temp. (°C)
7.5	5	25	5	90

3. Post processing

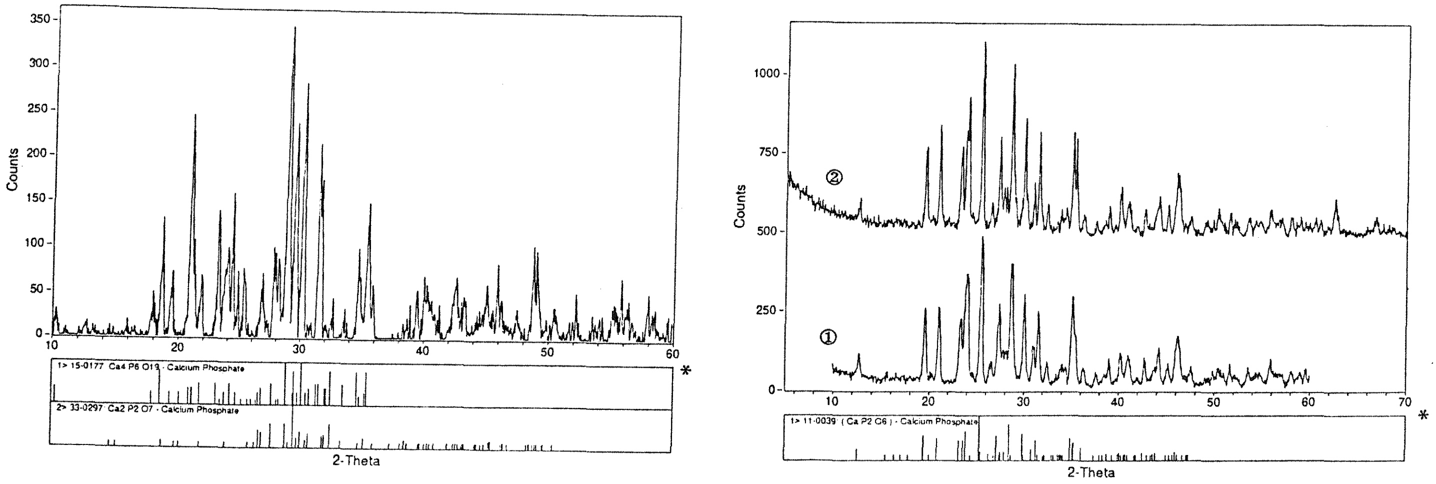
(1) Firing The green parts are fired up to sintering temperature to remove the polymer and subsequently to sinter. The temperature was raised at the average rate of 16°C/min up to 500°C and then raised slowly to 880°C. The parts were held at 880°C for 2 hours and cooled down slowly. During the firing, the parts were kept in lightly packed HA powder to help maintain the shape and provide even heat distribution to reduce curling. HA was chosen as packing material due to its low bulk density, less than 0.5 g/cm^3 and high melting temperature. Low density material is critical when fire the complex shape parts because thermal stress create cracks between layers. The fired polymer free parts are then infiltrated with calcium phosphate solution.

(2) Infiltration Infiltration of ceramic cement in a green structure was proposed as an alternative of high temperature sintering.[5] Due to the severe restriction imposed on selection of cement for biomedical applications, the calcium phosphate solution was chosen as the infiltrant. For the effective penetration through the pore, the calcium phosphate have to be dissolved completely in biologically acceptable media. In essence, calcium phosphate paste was prepared by mixing HA and phosphoric acid and then diluted by adding water to form slurry. The prepared slurry is dissolved in boiling water. It is found that 15g of HA with 60 g of 85 % phosphoric acid is good composition when dissolved in boiling water to make about 120 ml of solution. Complete thermal dehydration and condensation of this solution around 600°C forms non porous and transparent ultraphosphate glass that contains of

15.7% CaO. Infiltration is performed mainly by capillary action. After pores are saturated with infiltrant, the parts are allowed to dry and then fired at the appropriate temperature according to the expected final Ca/P ratio. It is found that when pores are saturated upon infiltration, the resulting weight gain is inversely proportional to the initial density.

Results and discussion

The SLS processed CMP green parts have density about 0.91 ±0.03 g/cm^3, 33 % of theoretical density with the fracture strength of 130 ±20 psi which is good enough to permit rough handling of complex bone shapes, such as that shown in Figure 2. This craniofacial image composed of 27 different layers was created from Computed Tomographic scans of a human temporal bone.[6] This part is approximately four inches long and one and half inch thick with very well defined cavities. However, 35CaP green parts have density of $0.83 g/cm^3$ with the fracture strength of 40 ± 10 psi . This relatively low strength of the latter parts are attributed to smaller particle size, consequently higher surface area of powder than that of CMP powder. In the powder preparing step, the firing temperature 900°C was sufficient to coalesce CMP, melting point of 985°C. However, for 35CaP powder, which has a higher melting temperature, 900°C was not high enough to coalesce the powder. The resulting powder has very high surface area. This reasoning is verified when CPP powder, fired at 1300 C for 2 hours, then ground in the attritor and classified to a mean diameter of $30 \mu m$, showed good green strength with 15 wt.% polymer whereas the powder fired at 900°C, ground to a mean diameter of $2 \mu m$, barely sintered at all. Also, 1NaCPP powder of surface area of 1.8 m^2/g was barely sintered and surface area of 1.4 m^2/g was sintered slightly with loose powder. Whereas the powder of surface area of 1.1 m^2/g showed very good strength.



(A)

(B)

Figure 1. X-ray diffraction patterns
(A) Pattern for 35CaP powder.
(B) À Pattern for CMP powder as prepared.
Á Pattern for 35CaP after infiltrated and fired.
* The standard patterns are presented in small box

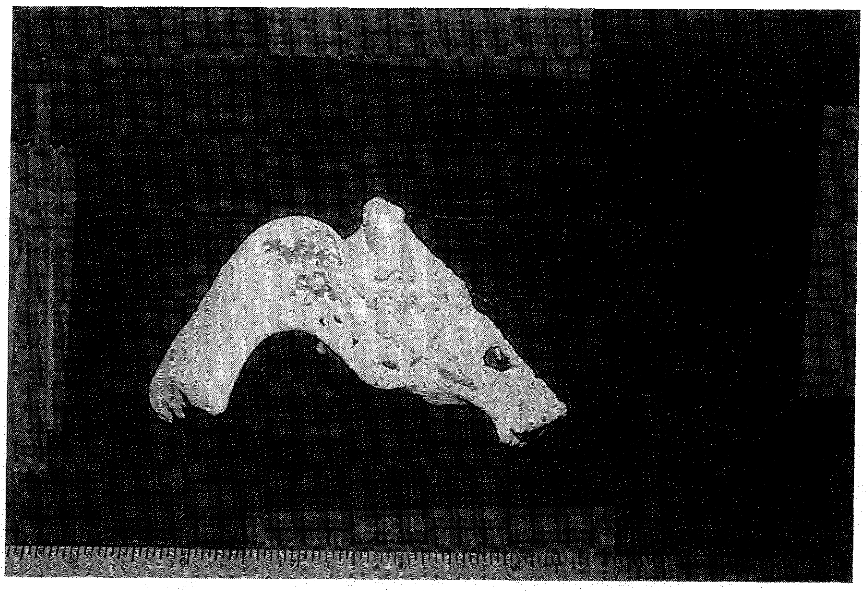


Figure 2. SLS processed craniofacial image from CMP powder.

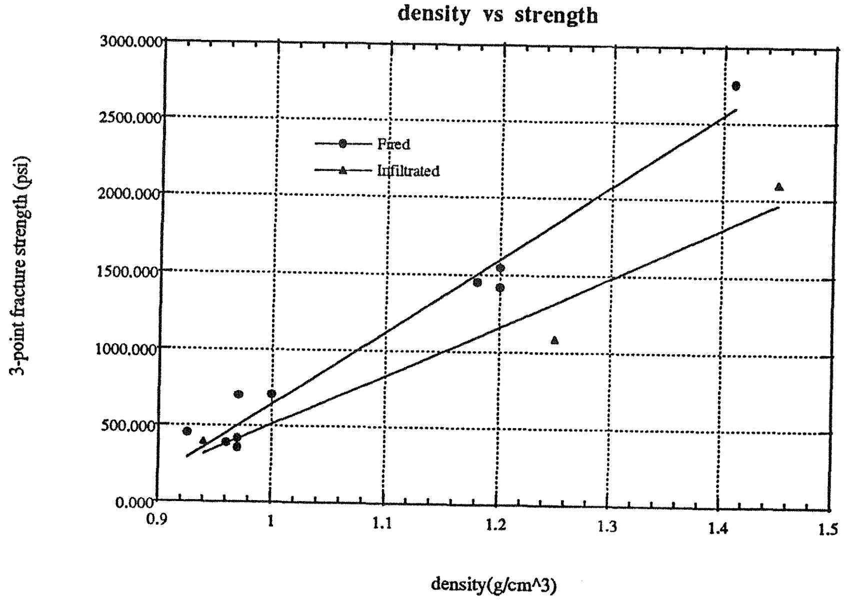
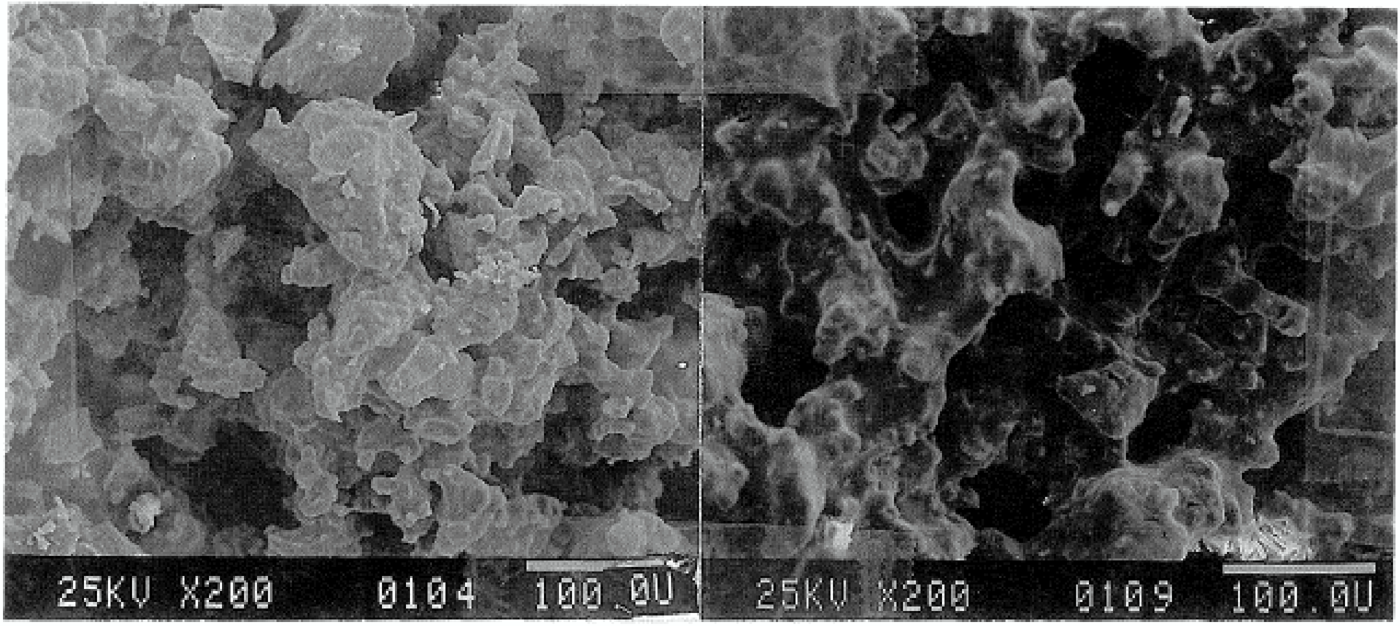


Figure 3. Three point bending strength VS. density of fired part and post processed part

CMP green parts were fired at 880°C for 2 hours. The fired CMP parts showed 3 point bending strength about 400 psi and a density of about 0.97g/cm^3, corresponding to a 17% volume shrinkage. And the strength of about 2700 psi part was obtained by firing at 940°C for 1 hour with a density of about 1.4g/cm^3. The polymer free parts with a density of about 0.97g/cm^3 were infiltrated as described earlier. For the CMP parts, first infiltration resulted in 31±2 % weight gain after firing 725°C and strength of 1100 psi and more infiltration increased the density about 50 % and strength about 1500 psi. Strength vs. density data are shown in figure 3. Further infiltration caused the parts to melt and deform inhomogeneously at 725°C, which could indicate existence of Ca/P concentration gradient through the part. This even lowered the strength of the part. The fractured surface of this part showed randomly distributed vitrified parts. It is believed that inflitrant, which is ultraphosphate, filled up the pore and formed a phosphate glass. This part were ground back to the powder for the X - ray diffraction analysis. There was no big noticeable difference in X - ray patterns between before and after infiltration. This indicating that no new crystalline phase had been formed. For the 35CaP fired part, the first infiltration caused about 40 % weight gain due to the lower green density, and further infiltration increased the strength to about 3500 psi . X - ray diffraction analysis indicate that



(A) (B)

Figure 4. Scanning Electron Micrographs of porous fractured surface (A) fired. (B) fired and infiltrated. (X 200)

initial powder which was mixture of major phase of $4CaO3P_2O_5$ and minor phase of CPP was converted to calcium metaphosphate after post processing. Figure 1 (B) shows this phase transformation. The morphology of the fired and infiltrated fracture surface are shown in Figure 4. It is noticeable that infiltration make the more necking between the grains. The pores are well interconnected and the pore size is approximately larger than 50 μm.

The firing step causes the part to shrink, which is not desirable because one of the purpose of the SLS for implant material is construction of the accurate facsimile bone structure from the geometric information obtained from patient computed tomography data. Even worse, the shrinkage is not isotropic. Linear shrinkage in thickness is much larger than that in width or length, due to the nature of layer-wise construction of parts in SLS process. In the attempt to avoid the shrinkage, it is proposed that infiltration should be performed on a green part while the polymer present.[7]

Conclusion

It has been shown that complex and delicate bone shape parts can be fabricated from CT data by using selective laser sintering process. It has also been shown that, in order to make denser porous calcium metaphosphate parts, calcium rich powder are SLS processed and calcium phosphate solution are then to be infiltrated to convert the parts to metaphosphate. However, there are still many problems to be investigated. Some of these problems are understanding of effect of the surface area and micro porosity on green strength, controlling the infiltration step to end up with metaphosphate composition according to Ca/P ratio of initial powder, and optimum firing temperature and cycle.

Acknowledgements

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