

A Novel Fabrication Technique of Porous Hydroxyapatite Ceramics

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The macroporous hydroxyapatite (HA) ceramics was fabricated by using the spark plasma sintering process (SPS). Calcium oxide with the controlled particle size was used as the pore forming material. HA did not react with CaO during the SPS process at 800°C for 10 min. CaO was suitable for the pore forming material to fabricate macroporous HA ceramics. CaO in HA/CaO composite could be removed by treating in the saturated NH₄Cl aqueous solution. Although the sintering temperature is about 300 °C lower than other method, the flexural strength of the porous HA fabricated in this study was comparable to previous reports.

Key words: Hydroxyapatite, Calcium Oxide, Spark Plasma Sintering, Porous Ceramics

1. INTRODUCTION

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HA) is inorganic principal constituent of hard tissue such as bone or teeth. HA is an attractive material as an artificial bone because of its biocompatibility, bioactivity and osteoconductivity. HA ceramics are used in various forms such as compact materials, porous materials and granular particles *etc.* Among these forms, macroporous HA ceramics are important because its porous network allows the tissue to infiltrate, which further enhances the implant tissue attachment [1, 2]. The pore must be larger than 100 μm according to some researchers [2-4].

On the other hand, spark plasma sintering (SPS) technique recently attracts attentions as a new sintering process because the sintering is possible at lower temperature and in a shorter duration than the conventional sintering processes. The application of SPS to HA is beginning to be reported recently. Gu et al. has reported that the HA powder was sintered to near theoretical density (99.6%) at 950 °C for 5 min [5]. Ioku et al. has reported that the transparent hydroxyapatite ceramics were prepared by SPS process at 900 °C for 10 min [6]. Thus SPS is suitable to produce dense materials. However, there are few reports of production of porous material, especially

macroporous materials, by SPS process. This is because SPS process is pressure sintering.

In this study, the fabrication of the macroporous hydroxyapatite ceramics was tried by using the spark plasma sintering process.

2. EXPERIMENTAL

Figure 1 shows the flow chart of experimental procedure. In this study, calcium oxide (CaO) was used as the pore forming material because of 1) its high melting point (2570 °C), 2) solubility in NH₄Cl aqueous solution and 3) its no toxicity. Calcium

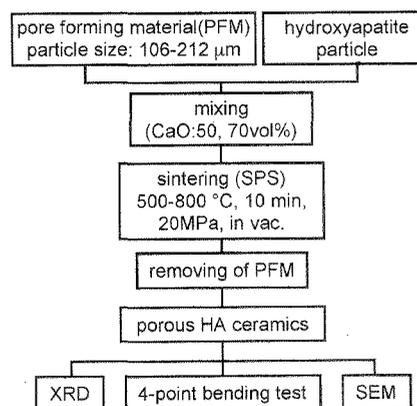


Fig.1 Flow chart for the fabrication of macroporous hydroxyapatite ceramics.

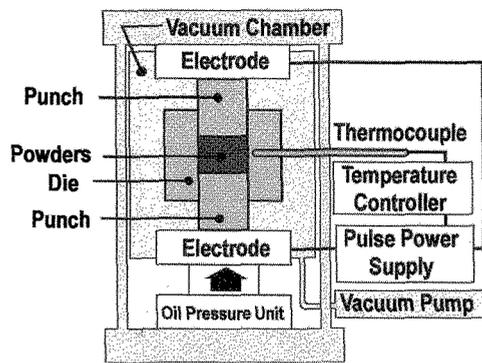


Fig.2 Schematic illustration of spark plasma sintering system.

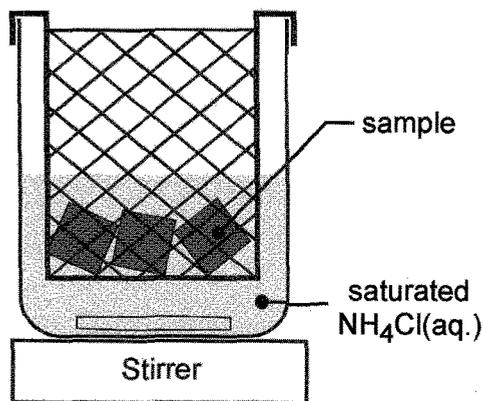


Fig.3 Schematic illustration of dissolution apparatus of the pore forming material.

carbonate (Kojundo Chemical Lab Co., Ltd) was decarbonated by calcining at 1000 °C for 1 h. The obtained CaO was SPSed at 700 °C for 3 min, and then ground to a powder. The CaO powder was sieved at from 106 to 212 μm.

HA particles (average particle size: 10 μm, Ube Materials Industries, Ltd.) were mixed with the pore forming particles (CaO), and the mixing ratio of the pore forming particles was 50 and 70 vol%. The mixed powder of about 1 g was poured into a graphite die (inner diameter 15 mm), and then sintered by spark plasma sintering system (Izumi Technology Company, Ltd., SPS-520, Fig.2) in the range from 500 to 800 °C for 10 min with heating rate of 100 °C/min in vacuum. The temperature was measured by thermocouple at the graphite die. The samples were pressed uniaxially under 20 MPa.

The sintered compacts were cut in size of 5x5x2 mm by a diamond saw, and then the CaO in the compact was dissolved into a saturated NH₄Cl aqueous solution at room temperature (Fig.3). The

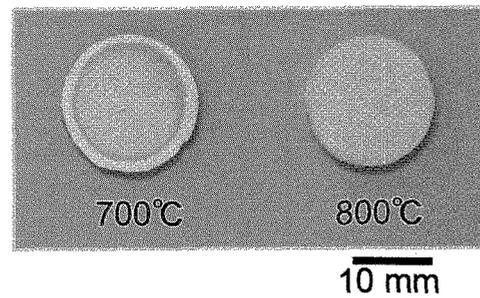


Fig.4 Photographs of HA/CaO composite ceramics SPSed at (a) 700°C and (b) 800°C.

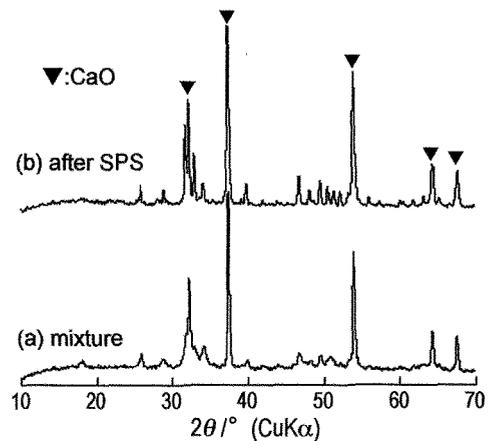


Fig.5 XRD patterns of (a) mixed HA/CaO powders and (b) HA/CaO composite after spark plasma sintering at 800 °C for 10 min. The mixing ratio of CaO is 50vol%.

amount of residual CaO was checked by measuring the mass of sample.

The starting powder, the sintered compact and the obtained porous ceramics were identified by powder X-ray diffractometer (XRD). The flexural strength was measured in a four-point configuration with a top span length of 5.4 mm, bottom span length of 16.0 mm and crosshead speed of 0.5 mm/min. The specimens with the dimension of 2x3x18 mm were prepared from the sintered compact of 20 mmφ. The results of four measurements were averaged. The pore structure was observed by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1 Spark plasma sintering

The appearance photograph of the sintered HA/CaO composites was shown in Fig.4. The compact was densified only at its center when it was sintered at

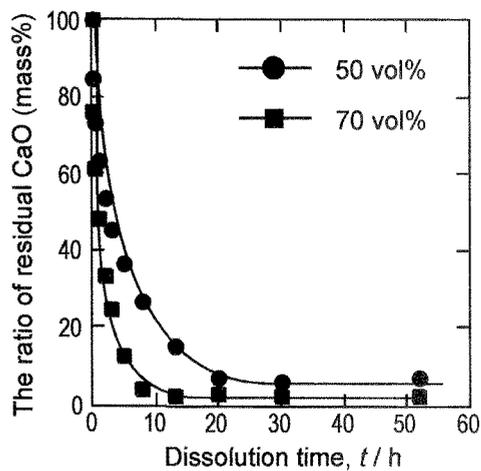


Fig.6 Dissolution behavior of CaO in HA/CaO composite into the saturated NH_4Cl aqueous solution. (a) 50vol%, (b) 70vol%

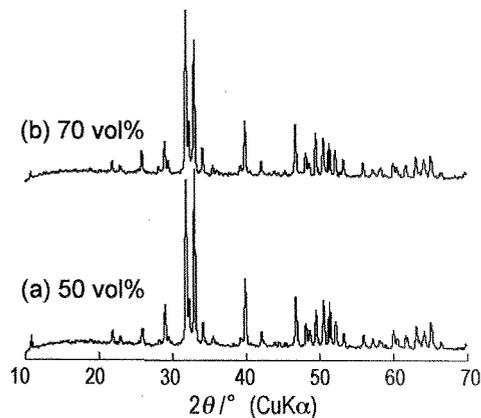


Fig.7 XRD patterns of the porous ceramics after dissolution for 52 h. (a) 50 vol% , (b) 70vol% .

700 °C for 10 min. It was not enough to densify the edge outside of the compact. It was easy to break. On the other hand, the compact was densified uniformly by processing at 800 °C for 10 min. The compacts was hardly densified below 600 °C, consequently, the compact was broken spontaneously after several days due to the volume expansion with the hydration of CaO. From these results, it was found that the compact could be sintered enough at 800 °C for 10 min.

Figure 5 shows the XRD patterns of mixed HA/CaO powders and HA/CaO composite after spark plasma sintering at 800 °C for 10 min. The XRD patterns before and after SPS did not change except for change in crystallinity of HA. These XRD patterns show that HA did not react with CaO. The same results were also obtained in the case of 70 vol% of CaO. CaO is suitable for the pore forming material to fabricate

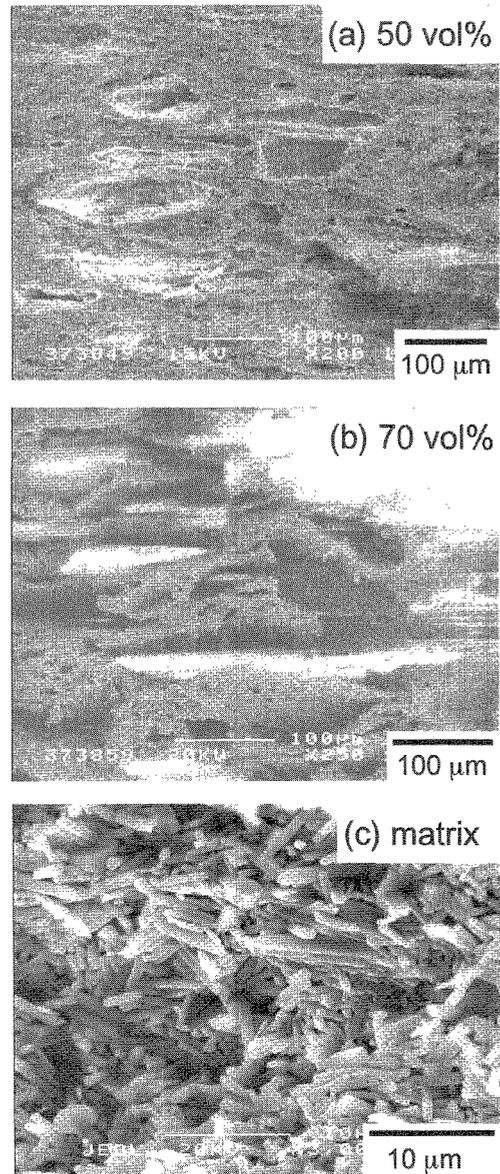


Fig.8 SEM photographs of the (a), (b) fracture of the porous HA ceramics and (c) matrix. (a) 50 vol% , (b) 70vol% .

macroporous HA ceramics.

3.2 Dissolution of the pore forming material

Figure 6 shows the dissolution behavior of the pore forming material CaO. Axis of ordinate and abscissa show the ratio of residual CaO calculated from the mass measurement and the dissolution time, respectively. For the HA/CaO composite with 70 vol% of CaO, the dissolution of CaO was almost finished in 12 h. For the HA/CaO composite with 50 vol% of CaO, the dissolution of CaO was almost finished in 24 h. The composite with high mixing ratio of CaO showed faster dissolution than that of low one. The reason

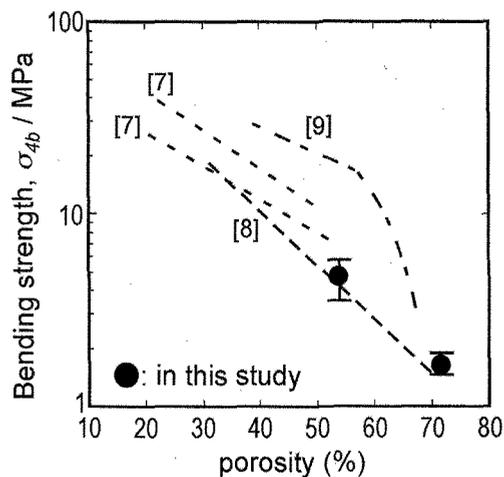


Fig.9 The flexural strength of the porous HA ceramics fabricated in this study and reference values[7-9] .

would be that CaO particles in HA/CaO with 70 vol% CaO form a close packed structure (filling ratio: about 74 vol%). That is, the dissolution path of CaO was secured sufficiently, consequently it results in the fast dissolution of CaO.

The XRD patterns of the porous ceramics after the dissolution for 52 h are shown in Fig. 7. The fabricated porous ceramics consisted of hydroxyapatite only. These results indicated that CaO could be removed completely from HA/CaO composite by using the saturated NH_4Cl aqueous solution.

3.3 Characterization of porous HA ceramics

The SEM photographs of the fracture of fabricated porous HA ceramics are shown in Fig.8. The pore size of the fabricated porous HA ceramics was similar to the pristine CaO particle size. However, the pores were slightly deformed in the direction of compressive stress. The matrix of porous HA ceramics was made up of small crystals of several micrometer (Fig.8 (c)).

Figure 9 shows the four-point bending strength. Ordinate and abscissa show the flexural strength in logarithmic scale and the porosity, respectively. The dotted lines show the data from references [7-9]. The flexural strength of the porous HA ceramics with the porosity of 50 and 70 vol% was about 5 and 1 MPa, respectively. The fabrication temperatures in other reports are in the ranges from 1150 to 1300 °C. Although the sintering temperature in this study is about 300 °C lower than that of other researches, the flexural strength was comparable to those in other

reports.

4. CONCLUSIONS

The fabrication of the macroporous hydroxyapatite ceramics was tried by using the spark plasma sintering process. The results described in this paper allow to draw the following conclusions.

(1) The porous HA ceramics can be fabricated by spark plasma sintering. Calcium oxide was suitable for the pore forming material.

(2) Calcium oxide in the HA/CaO composite can be removed by treating the saturated NH_4Cl aqueous solution.

(3) Although the sintering temperature in this study is lower than those in the previous researches, the flexural strength was similar.

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