

## Preparation of Porous Hydroxyapatite Ceramics by Spark Plasma Sintering

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Hydroxyapatite (HA),  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , is one of the most biocompatible materials for human bones. HA is promising bone substitute material for clinical application because of clinical stability *in vivo*. Porous HA scaffolds have attracted a considerable attention for biomedical engineering applications. The objective of this study is to prepare the samples to HA scaffold ceramics for the human cells. Porous HA ceramics was prepared by spark plasma sintering (SPS) at the temperatures from 400°C for 10 min with a heating rate of 25 K min<sup>-1</sup>. The aramid fiber in ceramics prepared by SPS was burned away during firing at 500°C 1 h in air. The porous HA ceramics prepared by SPS at 400°C had macro pore. Average pore size of the ceramics sintered by SPS method at 400°C was around 15 μm in size. There were almost no pores in the matrix of HA ceramics by SPS method. The measured compressive strength of porous HA scaffold was 40 MPa with a porosity of 30%. These results proved that SPS is a potential method for fabricating porous HA ceramics at the much lower temperature than conventional methods.

Key words: hydroxyapatite, spark plasma sintering, scaffold, biocompatibility

### 1. INTRODUCTION

Hydroxyapatite (HA),  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , has the attractive feature of biocompatibility for the human hard tissue, therefore, many clinical applications of HA were carried out as artificial bones and teeth roots [1-4]. Several previous studies have also confirmed that HA is a stable material *in vivo* [5-6].

Porous ceramics have been investigated in several application fields such as biomaterial, filter, adsorbent and separation. In biomedical application, porous HA materials have been known to be biocompatible and osteoconductive [7]. Porous HA scaffolds have attracted a considerable attention for biomedical engineering applications. It is well known that the pore structure of porous scaffold strongly affects its mechanical properties and biological performance. The macroporous ceramics also requires control of pore sizes, shapes and pore size distribution in order to design preferred physical and chemical properties. Many methods have been used to manufacture porous ceramics. Conventional methods include the addition of a pore-former such as an organic material that burns away during firing.

An innovative powder densification technology known as spark plasma sintering (SPS) has been developed in recent years. The SPS process is a synthesis and processing technique which makes it possible to sinter at low temperature and in a short period by charging the intervals between powder particles with electrical energy and effectively applying high temperature spark plasma generated momentarily [8-9]. SPS can be an effective method to prepare HA ceramics [10-11]. Kawagoe and Ioku reported that transparent HA ceramics and β-tricalcium phosphate ceramics were prepared by SPS at 900°C and 1000°C

for 10 min [12-17].

In the present study, porous HA ceramics were prepared by spark plasma sintering (SPS) at the temperatures from 400°C for 10 min with a heating rate of 25 K min<sup>-1</sup> in vacuum. It has the possibility that aramid fibers maintain the shape of pore in green compact after sintering in SPS at 400°C, therefore aramid fiber was used.

In this study, porous HA ceramics for strong scaffold were prepared using aramid fibers by SPS.

### 2. EXPERIMENTAL PROCEDURE

#### 2.1 Sintering Process

Fine powder of HA (High-purity grade Ube Materials, Co. Ltd., Japan) was used as the starting material. Aramid fiber K49 (DU PONT-TORAY) was used (Table I) as an organic material to make pores in HA.

HA powders (0.42 g) was mixed with aramid fibers (0.08 g). The mixed powders were uniaxially pressed into tablets, 15 mm in diameter, with a pressure of 160 MPa. The obtained tablets were sintered at 900°C for 3 h in air.

HA powders (0.42 g) and the organic material (0.08 g) were poured into the graphite mold (inner diameter 10 mm), and then sintered by SPS method (SPS: Dr Sinter-511S, Sumitomo Coal Mining, Co. Ltd., Japan) (see Fig.1). The temperatures of the samples during sintering were measured by thermocouples of Rh/Pt-Pt which was inserted into the wall of the graphite mold to measure the sample temperature. The samples were pressed uniaxially under 30 MPa, and then they were heated at 400°C 10 min with a heating rate of 25 K min<sup>-1</sup>. The aramid fiber in ceramics prepared by SPS was burned away during firing at 500°C for 1 h in air.

## 2.2 Characterization

The starting powder and the obtained ceramics were identified by powder X-ray diffractometer with graphite-monochromatized  $\text{CuK}\alpha$  radiation, operated at 40 kV and 20 mA (XRD; MXP3, MAC Science Co. Ltd., Japan). The obtained ceramics were polished with 4000-grid SiC. Density measurements based on Archimedes' principle were conducted. Theoretical density of HA was assumed to be  $3.16 \text{ g}\cdot\text{cm}^{-3}$ . The surface and internal structure of ceramics was observed by means of scanning electron microscopy (SEM; S-2100A, Hitachi High-Technology Corporation, Japan). Thermogravimetry and differential thermal analysis (DTG; DTG-50H Shimadzu Corporation, Japan) was executed under the following condition: 10 mg of samples,  $\alpha\text{-Al}_2\text{O}_3$  reference, and a heating rate of  $10 \text{ K}\cdot\text{min}^{-1}$  from room temperature to  $900^\circ\text{C}$ . The compressive strength of porous ceramics was measured by mechanical testing machine (Universal Testing Machine; AG-M1 50kN, Shimadzu Corporation, Japan).

Table I Details of the organic material.

Type	Source	Decomposition Temperature
Aramid fiber	K49 DU PONT -TORAY	About $500^\circ\text{C}$

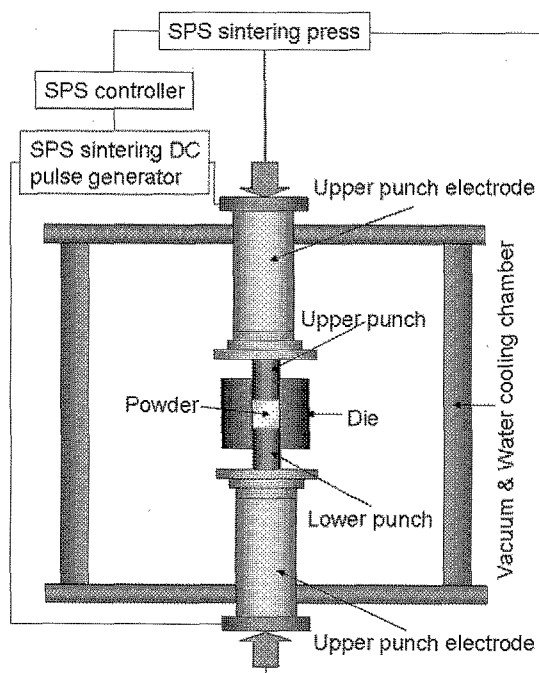


Fig. 1 Schematic representation of spark plasma sintering system.

## 3. RESULTS AND DISCUSSION

Figure 2 shows the thermogravimetric curve of the composite particles consisting of the aramid fibers and HA particle. The weight rapidly decreased around  $480^\circ\text{C}$  due to decomposition of aramid fibers. The aramid fibers decomposed completely before  $640^\circ\text{C}$ . Further weight loss could not be detected from  $640^\circ\text{C}$  to  $900^\circ\text{C}$ .

Thus the heat treatment temperature of  $900^\circ\text{C}$  is high enough to decompose the aramid fibers from porous ceramics by conventional method.

The density of green compact, ceramics prepared by normal sintering and ceramics prepared by SPS were measured. Average relative density of the green compact was approximately 43%. Average relative density of the ceramics prepared by normal sintering at  $900^\circ\text{C}$  for 3 h in air was approximately 36%. Average relative density of the ceramics prepared by SPS at  $400^\circ\text{C}$  for 10 min was approximately 40%.

In the sintering process by SPS in this study, the densification was not started at about  $400^\circ\text{C}$  (see Fig. 3). It was reported that in the sintering process by SPS, the densification started at about  $600^\circ\text{C}$ , and then proceeded with increasing temperature to result in line shrinkage of about 40% at  $900^\circ\text{C}$ , which means the end of densification [13].

No other phase except for HA were revealed by XRD for the starting samples, samples after normal sintering at  $900^\circ\text{C}$  for 3 h and samples after sintering by SPS at  $400^\circ\text{C}$  for 10 min (no Figure).

The obtained ceramics were cut into two and the fracture surface was polished with 4000-grid SiC. According to the SEM observation result, the ceramics prepared by normal sintering at  $900^\circ\text{C}$  had pores of about  $0.1 \mu\text{m}$  in HA matrix. There were no pores in the ceramics in HA matrix prepared by SPS at  $400^\circ\text{C}$ .

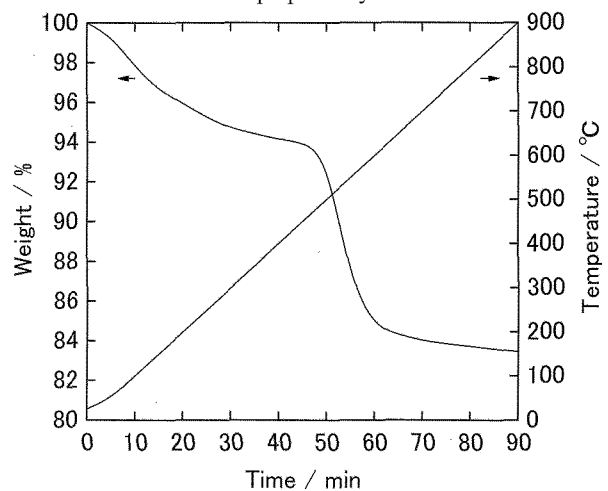


Fig. 2 Thermogravimetric curve of composite particles consisting of aramid fibers and hydroxyapatite at the heating rate of  $10 \text{ K}\cdot\text{min}^{-1}$  in air.

Average pore size of the ceramics sintered normally at  $900^\circ\text{C}$  for 3 h and sintered by SPS method at  $400^\circ\text{C}$  for 10 min were around  $15 \mu\text{m}$ . Therefore, there is a possibility that pores in green compact were designed by aramid fibers of  $15 \mu\text{m}$ . HA porous ceramics with macro-pores over  $100 \mu\text{m}$  in size are currently used as bone graft substitutes [18-21], because macro-pores allows cells to enter easily into the materials. With aramid fibers of  $100 \mu\text{m}$ , it must be possible to fabricate porous HA ceramics with macro pores of  $100 \mu\text{m}$ .

The measured compressive strength of HA prepared by SPS at  $400^\circ\text{C}$  for 10 min was 40 MPa with a porosity of 30%. This value is as high as that of HA prepared by

normal sintering at high temperature for long sintering time. All these results suggest that there is a possibility of fabrication of porous HA ceramics for scaffold by SPS method.

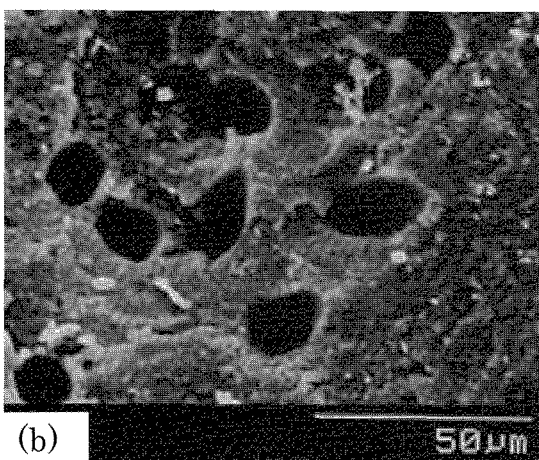
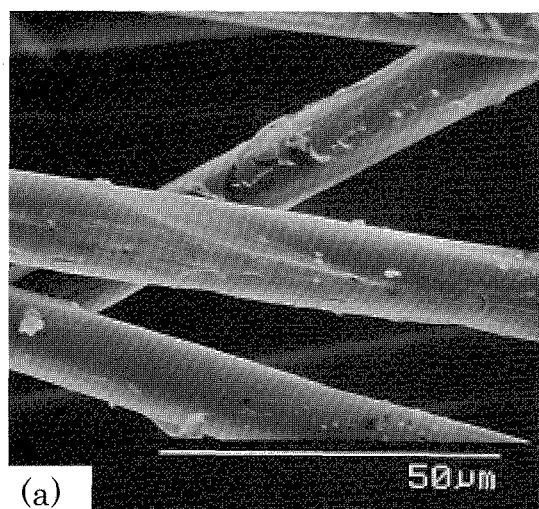


Fig. 3 SEM photographs of (a) aramid fibers and (b) HA ceramics prepared by SPS at 400°C for 10 min. Aramid fibers in ceramics were burned away at 500°C for 1 h in air.

#### 4. SUMMARY

Porous hydroxyapatite ceramics were prepared by spark plasma sintering at 400°C for 10 min.

#### 5. Acknowledgments

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#### 6. REFERENCES

- [1] K. Ioku, *J. Soc. Inorg. Mater. Jpn.*, **3**, 412-18 (1996).
- [2] A. Ito, X. Sun, *J. Soc. Inorg. Mater. Jpn.*, **3**, 386-91 (1996).
- [3] H. Aoki, "Medical Applications of Hydroxyapatite", Isiyaku Euro America, Inc., Tokyo and St. Louis (1994).
- [4] T. Kanazawa, T. Umegaki, H. Monma and K. Yamashita, *J. Soc. Inorg. Mater. Jpn.*, **210**, 261-73 (1987).
- [5] K. Ioku, K. Yanagisawa, N. Yamasaki, H. Kurosawa, K. Shibuya, H. Yokozeki and T. Hayashi, *Biomed. Mater. Eng.*, **3**, 137-45 (1993).
- [6] K. Ioku, H. Kurosawa, K. Shibuya, H. Yokozeki and T. Hayashi, "Bioceramics 7", Ed. by O. H. Andersson and A. Yli-Urpo, Butterworth-Heinemann, (1994) pp. 97-102
- [7] M. Jarcho, *Clin. Orthop.*, **157**, 259- 78 (1981).
- [8] T. Nishimura, M. Mitomo, H. Hirotsuru and M. Kawahara, *J. Mater. Sci. Lett.*, **14**, 1046-47 (1995).
- [9] M. Tokita, *J. Soc. Powder Technol. Jpn.*, **30**, 790-804 (1993).
- [10] A. Nakahira, M. Tamai, H. Aritani, S. Nakamura and K. Yamashita, *J. Biomed. Mater. Res.*, **62**, 550-57 (2002).
- [11] Y.W.Gu, N.H.Loh, K.A.Khor, S.B.Tor and P. Cheang, *Biomaterials*, **23**, 34-37 (2002).
- [12] D. Kawagoe, K. Ioku, H. Fujimori and S. Goto, *J. Ceram. Soc. Jpn.*, **112**, 462-63 (2004).
- [13] D. Kawagoe, K. Ioku, H. Fujimori and S. Goto, *Trans. Mater. Res. Soc. Jpn.*, **28**, 841-44 (2003).
- [14] D. Kawagoe, K. Ioku, H. Fujimori and S. Goto, "Hydrothermal Reactions and Techniques", Ed. by S. H. Feng, J. S. Chen and Z. Shi, World Science, New Jersey, London, Singapore, Shanghai, Hong Kong, Taipei, Bangalore (2003) pp. 115-20.
- [15] K. Ioku, D. Kawagoe, H. Toya, H. Fujimori, S. Goto, K. Ishida, A. Mikuni and H. Mae, *Trans. Mater. Res. Soc. Jpn.*, **27**, 447-49 (2002).
- [16] N. Kotobuki, D. Kawagoe, N. Daishirou, Y. Katou, K. Murakami, H. Fujimori, S. Goto, K. Ioku and H. Ohgushi, *J. Mater. Sci. Mater. Med.*, **17**, 33-41 (2006).
- [17] N. Kotobuki, K. Ioku, D. Kawagoe, H. Fujimori, S. Goto and H. Ohgushi, *Biomaterials*, **26**, 779-85 (2005).
- [18] R. A. Finn, W. H. Bell and J. A. Brammer, *J. Max. Fac. Surg.*, **8** 217- 27 (1980).
- [19] R. M. Meffert, J. R. Thomas, K. M. Hamilton and C. N. Brownstein, *J. Periodontol.*, **56**, 63- 74 (1985).
- [20] K. Ioku, *J. Soc. Inorg. Mater. Jpn.*, **3**, 412-18 (1996).
- [21] K. Ioku, *J. Soc. Inorg. Mater. Jpn.*, **8**, 153-59 (2001).

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