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# Densification Process of OH Controlled Hydroxyapatite Ceramics by Spark Plasma Sintering

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**Abstract.** Calcium hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\text{-HA}$ , is the inorganic principle component of natural bones and teeth. It has been already suggested that the amount of OH ion in the crystal structure of HA is closely related to the biocompatibility. The amount of OH ion in current HA, however, has not been controlled. In order to prepare more functional HA ceramics, the amount of OH ion must be controlled. In this study, HA ceramics with different OH amount were prepared from fine HA crystals by spark plasma sintering (SPS). In order to reveal the ideal sintering conditions for preparation of transparent ceramics, densification process on SPS was investigated. The samples were pressed uniaxially under 60 MPa, and then they were heated by SPS at 800 °C, 900 °C and 1000 °C for 10 min with the heating rate of 25 °C·min<sup>-1</sup>. The quantity of OH ion in HA ceramics sintered by SPS was decreased with increasing temperature of sintering. Transparent HA ceramics were prepared by SPS at 900 °C and 1000 °C. In analysis of the densification behavior during sintering of HA by SPS, dominant sintering mechanism was plastic flow of densification. Transparent ceramics should be the most suitable materials to investigate the interface between human cells and ceramics.

**Keywords:** Hydroxyapatite, Transparent ceramics, Spark plasma sintering and Plastic flow

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## INTRODUCTION

Calcium hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\text{-HA}$ , is the inorganic principle component of natural bones and teeth. This material 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 [1-5].

It has been already suggested that the amount of OH ion in the crystal structure of HA is closely related to the biocompatibility, the ability for bone formation and the ionic conductivity. The amount of OH ion in current HA, however, has not been controlled [6]. In the past papers, Fujimori and Ioku et al. reported that the amount of OH ion in HA was controllable by the control of heating conditions [7].

Comparing to the conventional sintering, spark plasma sintering (SPS) enables the ceramics to densify at lower temperatures and shorter duration by charging the intervals among powder particles with electrical energy and efficiently applying a high temperature spark plasma momentarily [8-9]. SPS can be an effective method to prepare HA ceramics [10-11].

The present study deals with the preparation of HA ceramics with a different OH amount by SPS.

The second objective of this study is preparation of the ideal samples to investigate the behavior of human cells on the surface of ceramics of HA. Direct observation of cultured cells on various materials has benefit for assessment of fundamental cellular functions including cell attachment, spreading, proliferation and differentiation on the materials.

In this study, to reveal the ideal sintering conditions for preparation of transparent ceramics, effects of plastic flow on SPS were investigated.

## SINTERING PROCESS

HA powder (High-purity grade, Ube Materials, Japan) of about 0.5 g was poured into a graphite mold (inner diameter 8 mm), and then sintered by SPS method (SPS: Dr. Sinter-511S, Sumitomo Coal Mining, Japan). The temperature of samples during sintering were measured by thermocouples of Rh/Pt-Pt, they were inserted into the wall of the graphite mold to measure the sample temperature. The samples were pressed under 60 MPa, and then they were heated at 800 °C, 900 °C and 1000 °C for 10 min with a heating rate of 25 °C·min<sup>-1</sup>.

## CHARACTERIZATION

The starting powder and the obtained ceramics were identified by a powder X-ray diffractometer with graphite-monochromatized CuK $\alpha$  radiation, operated at 40 kV and 20 mA (XRD; Geiger flex 2027, Rigaku, Japan). The morphology of particles was observed by transmission electron microscopy. The ceramics were polished with using a 4000-grid SiC and then polished finely with using a paste containing  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> fine particles smaller than 0.5  $\mu$ m in size. Density measurements based on Archimedes' principle were conducted. Theoretical density of HA was assumed to be 3.16 g·cm<sup>-3</sup>. The hardness of samples was evaluated by an indentation method using the Vickers hardness tester (Model AVK-AII; Akashi, Japan) at the load of 3 N for 10 s. The amount of OH ion in the ceramics was analyzed quantitatively by nuclear magnetic resonance (FT-NMR; Chemagnetics CMX300, Div. of Varian) and infrared spectroscopy (FT-IR; Spectrum 2000, Perkin Elmer). Thermogravimetry-differential thermal analysis (TG-DTA; TG-DTA32, Seiko Instruments Inc. Japan) was executed under the following condition:  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> reference, and a heating rate of 10 °C·min<sup>-1</sup> from room temperature to 1200 °C.

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From the densification behavior of HA during sintering by SPS,  $\ln(1 - D)$  were plotted against sintering period according to the Murray's equations [12-14] on SPS at 800 °C.

$$\ln(1 - ) = -\frac{3}{4} t + C \quad (1)$$

where D is relative density,  $\sigma$  is applied stress, n is viscosity coefficient, t is hold time and C is constant.

## RESULT & DISCUSSIONS

The quantitative chemical analysis gave a Ca/P molar ratio very closed to the correct HA stoichiometry (Ca/P=1.67). There were little

impurities as follows; Sr<8.9, Si<6.6, Mg<6.0, Na<5.0, K<5.0, Fe<0.9, Cu<0.7, Mn<0.2, Ba<0.1, Ni<0.1, Cd<0.1 ppm. The particle size along long axis of HA powder was less than 0.1  $\mu$ m by TEM observation (Fig. 1). The size and shape of particles were relatively homogeneous.

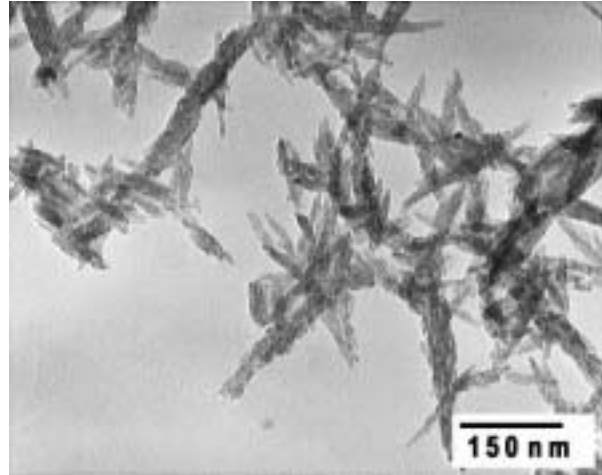


FIGURE 1. TEM photograph of starting powder of HA.

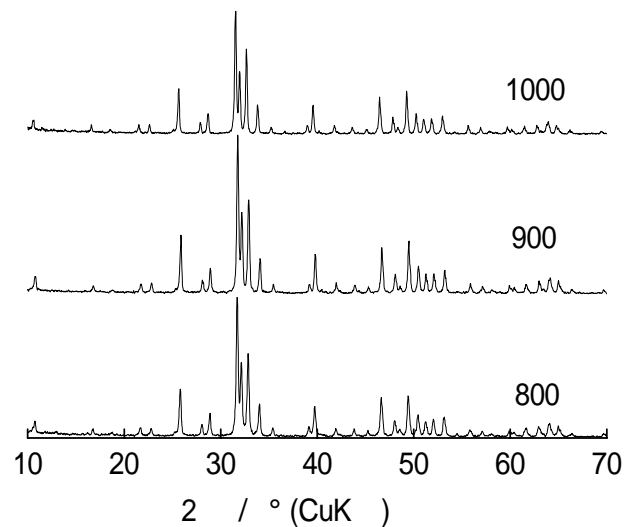


FIGURE 2. XRD patterns of HA ceramics prepared by SPS at 800 °C, 900 °C and 1000 °C.

No phases other than HA were revealed by XRD for the starting samples and samples after sintering by SPS at 800 °C, 900 °C and 1000 °C for 10 min (Fig. 2). The spectrum of FT-IR indicates the presence of OH<sup>-</sup> in the starting powder and also in the prepared

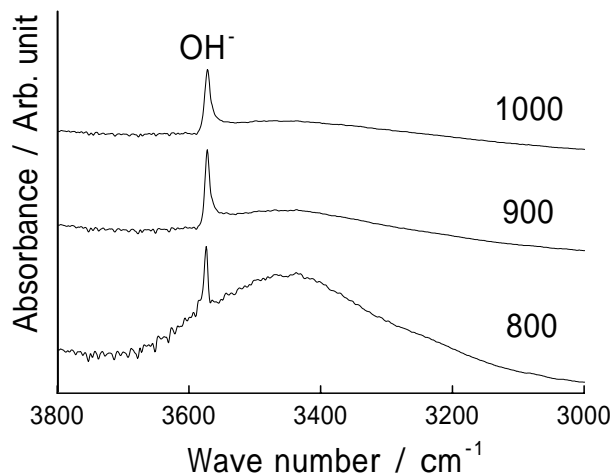
ceramics (Fig. 3). The band due to the stretching vibrations of OH ion appears at  $3571\text{cm}^{-1}$  [15]. The quantity of OH in HA ceramics sintered by SPS was decreased with increasing temperature of sintering. According to FT-IR and TG-DTA, the HA ceramics prepared at  $800\text{ }^{\circ}\text{C}$  was OH fully containing hydroxyapatite and the ceramics prepared at  $900\text{ }^{\circ}\text{C}$  was oxyhydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{1.2}\text{O}_{0.4}$ , where is a neutral vacancy in the OH site).

In the sintering process by SPS, the densification started at about  $630\text{ }^{\circ}\text{C}$ , and then proceeded with increasing temperature to result in line shrinkage of about  $2.2\text{ mm}$  at  $900\text{ }^{\circ}\text{C}$  (Fig. 4), which means the end of densification. The HA ceramics sintered by SPS at  $800\text{ }^{\circ}\text{C}$  showed about  $90\%$  relative density, and the ceramics sintered at  $900\text{ }^{\circ}\text{C}$  and  $1000\text{ }^{\circ}\text{C}$  showed over  $99\%$  relative density. Whereas in the case of normal sintering in air, densification started at about  $900\text{ }^{\circ}\text{C}$  [16]. These results proved that SPS is a potential method for fabricating highly dense HA ceramics at the much lower temperature like hot-pressing (HP) and hot isostatic pressing (HIP) [17-20]. In particular, sintering period is quite short time. Transparent HA ceramics were obtained by SPS at  $900\text{ }^{\circ}\text{C}$  and  $1000\text{ }^{\circ}\text{C}$  for  $10\text{ min}$  (Fig. 5).

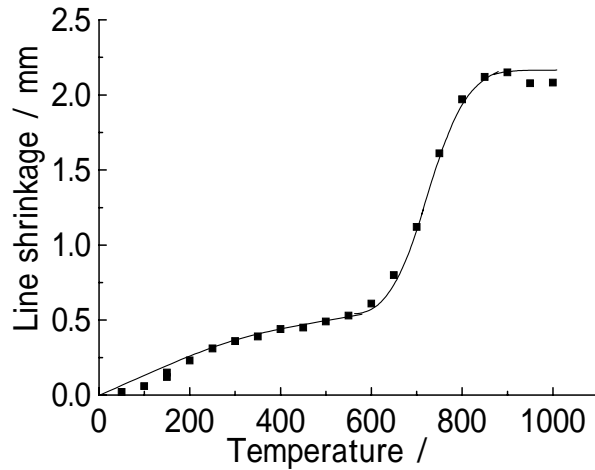
In analysis of densification process of HA on SPS (Fig. 6), dominant sintering mechanism of SPS was plastic flow in early stage of densification. Transparent HA ceramics should be the most suitable materials to investigate the interface between human cells and ceramics [21].

The amount of OH ion in the structure of hydroxyapatite was decreased with increasing temperature of sintering.

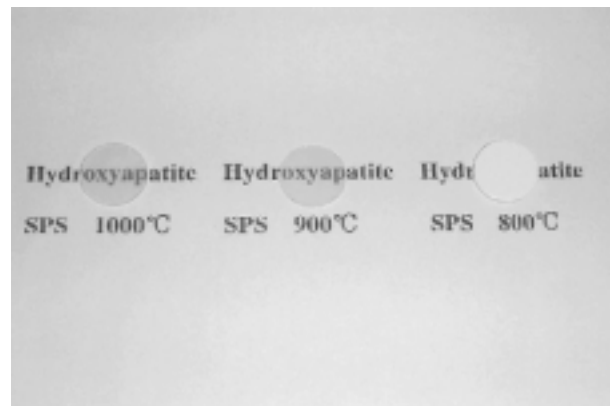
In analysis of plastic flow of HA on SPS, dominant sintering mechanism of SPS was plastic flow in early stage of densification.



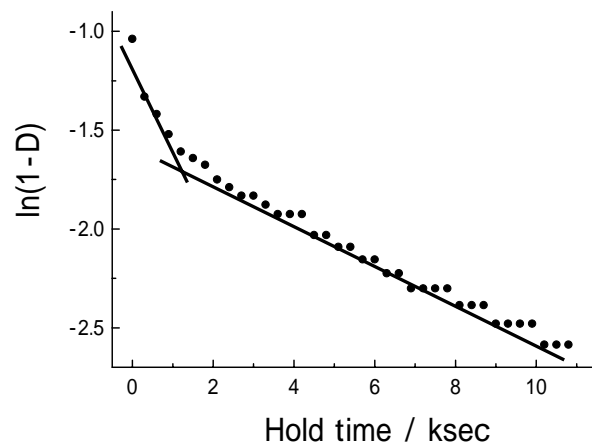
**FIGURE 3.** IR spectra of HA ceramics prepared by SPS at  $800\text{ }^{\circ}\text{C}$ ,  $900\text{ }^{\circ}\text{C}$  and  $1000\text{ }^{\circ}\text{C}$ .



**FIGURE 4.** Line shrinkage of HA at the indicated temperatures by SPS.



**FIGURE 5.** OH-controlled HA ceramics prepared by SPS at  $800\text{ }^{\circ}\text{C}$ ,  $900\text{ }^{\circ}\text{C}$  and  $1000\text{ }^{\circ}\text{C}$ .



**FIGURE 6.** Isothermal shrinkage behavior of HA heated at  $800\text{ }^{\circ}\text{C}$  by SPS.

## CONCLUSIONS

Transparent hydroxyapatite ceramics were prepared by SPS at 900 °C and 1000 °C.

## ACKNOWLEDGMENTS

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## REFERENCES

1. H. Aoki, in Medical Applications of hydroxyapatite, (Ishiyaku Euro America, Tokyo and St. Louis, 1994).
2. A. Ito and X. Sun, *J. Soc. Inorg. Mater. Japan (Muki-Materiaru)*, **3**, 386 (1996).
3. K. Ioku, *J. Soc. Inorg. Mater. Japan*, **3**, 412 (1996).
4. T. Kanazawa, T. Umegaki, H. Monma and K. Yamashita, *J. Soc. Inorg. Mater. Japan (Gypsum & Lime)*, 210, 261 (1987).
5. T. Kanazawa, T. Umegaki and H. Monma, *Ceramics*, **10**, 461 (1975).
6. K. Ioku, *Chem. Ind.*, **52**, 360 (2001).
7. H. Fujimori, H. Toya, K. Ioku, S. Goto and M. Yoshimura, *Chem. Phys. Lett.*, 325, 383 (2000).
8. T. Nishimura, M. Mitomo, H. Hirotsuru and M. Kawahara, *J. Mater. Sci. Lett.*, 14, 1046 (1995).
9. M. Tokita, *J. Soc. Powder Technol. Japan*, **30**, 790 (1993).
10. A. Nakahira, M. Tamai, H. Aritani, S. Nakamura and K. Yamashita, *J. Biomed. Mater. Res.*, **62**, 550 (2002).
11. Y.W.Gu, N.H.Loh, K.A.Khor, S.B.Tor and P. Cheang, *Biomaterials*, **23**, 37 (2002).
12. M. Kinoshita and Y. Hamano, *Yogyo-Kyokai-shi*, **80**, 239 (1972).
13. K. Umeya, T. Nishikawa and H. Nakajima, *J. Ceram. Assoc. Japan*, **75**, 301 (1967).
14. T. Shimohira, *Yogyo-Kyokai-shi*, **79**, 132 (1971).
15. S. Zhang, K. E. Gonsalves, *J. Mater. Sci. Mater. Med.*, **8**, 25 (1997).
16. K. Daimon, W. Min, T. Sugita, Y. Hikichi, T. Matsubara, T. Ota and Y. Kaji, *J. Soc. Inorg. Mater. Japan*, **8**, 283, (2001).
17. K. Ioku, M. Yoshimura and S. Somiya, *J. Ceram. Soc. Japan*, **96**, 109 (1988).
18. K. Ioku, S. Somiya and M. Yoshimura, *J. Mater. Sci. Lett.*, 8, 1230 (1989).
19. K. Ioku, M. Yoshimura and S. Somiya, *Biomaterials*, **11**, 57 (1990).
20. K. Ioku and M. Yoshimura: in Hot Isostatic Pressing: Theory and Applications (Elsevier Applied Science, London and New York, 1992).
21. N. Kotobuki, K. Ioku, D. Kawagoe, D. Nomura, H. Fujimori, S. Goto and H. Ohgushi, *Key Engineering Materials*, **284**, 663 (2005).