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Transparent Hydroxyapatite and β-Tricalcium Phosphate Ceramics Prepared by Spark Plasma Sintering

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Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) and β-tricalcium phosphate ($Ca_3(PO_4)_2$, β-TCP) are one of the most biocompatible materials with human bones. HA is promising bone substitute materials for clinical application because of clinical stability *in vivo*, while β-TCP has higher resorbability than HA when the materials is implanted in a bone defect. In this study, HA and β-TCP ceramics were prepared by spark plasma sintering (SPS) at the temperatures from 800 °C to 1000 °C for 10 min with a heating rate of 25 °C·min^{-1}. The HA ceramics prepared at 900 °C and 1000 °C showed transparency. The amount of OH ion in HA ceramics sintered by SPS was decreased with increasing temperature of sintering. Average grain size of the ceramics sintered at 900 °C was around 0.2 μm. The other hands, transparent β-TCP ceramics were obtained by SPS at 1000 °C for 10 min. Average grain size of the ceramics sintered at 1000 °C was around 1.5 μm. There were almost no pores in the transparent ceramics.

Key words: hydroxyapatite, β-tricalcium phosphate, spark plasma sintering, biocompatibility, transparent

1. INTRODUCTION

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) 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 [1-6]. 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 [7]. In order to prepare more functional HA ceramics, the amount of OH ion must be controlled. In the past paper, the authors suggested that the amount of OH ion in HA was controllable by the control of heating conditions [8].

Meanwhile, β-tricalcium phosphate (β-$Ca_3(PO_4)_2$, β-TCP) has higher resorbability than HA when the materials is implanted in a bone defect [9-13].

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 [14-16].

In this study, HA and β-TCP ceramics were prepared by SPS at the temperatures from 800 °C to 1000 °C for 10 min with a heating rate of 25 °C·min^{-1}. The objective of this study, is to prepare the ideal samples to investigate the behavior of human cells on the surface of ceramics of HA and β-TCP.

2. EXPERIMENTAL PROCEDURE

2.1 Sintering Process

Fine powder of HA (High-purity grade, Ube Materials, Japan) and fine powder of β-tricalcium phosphate (Taiheikagaku, Japan) were used as the starting material. These powders of about 0.5 g were poured into the graphite mold (inner diameter 15 mm), and then sintered by SPS method (SPS: Dr Sinter-511S, Sumitomo Coal Mining, Japan). The temperature of the samples during sintering were measured by thermocouples of Rh/Pt-Pt, it was inserted into the wall of the graphite mold to measure the sample temperature. The samples were pressed uniaxialy under 60 MPa, and then they were heated at 800 °C, 900 °C and 1000 °C for 10 min with the heating rate of 25 °C·min^{-1}.

2.2 Characterization

The starting powder and the obtained ceramics were identified by a powder X-ray diffractometer with graphite-monochromatized CuKα radiation, operated at 40 kV and 20 mA (XRD; Geiger flex 2027, Rigaku, Japan). The ceramics were polished with using a 4000-grid SiC and then polished finely with using a paste containing α-Al_2O_3 fine particles smaller than 0.5 μm in size. The hardness of ceramics was evaluated by an indentation method using the Vickers hardness tester (Model AVK-A II, Akashi, Japan) at the load of 3 N for 10 s. After thermal etching at the temperature below 10 °C sintering temperature for 10 min, surface of ceramics

was observed by using scanning probe microscopy (SPM; Nanopics 2100, Seiko Instruments, Japan). The amount of OH ion in the ceramics was analyzed quantitatively by infrared spectroscopy (FT-IR; Spectrum 2000, Perkin Elmer, USA). Thermogravimetry-differential thermal analysis (TG-DTA; TG-DTA 32, Seiko Instruments Inc., Japan) was executed under the following condition: α-Al_2O_3 reference, and a heating rate of 10 °C·min^{-1} from room temperature to 1200 °C.

3. RESULTS AND DISCUSSION

3.1 Transparent HA

No phases other than HA were revealed by XRD in the starting sample and the samples after sintering by SPS at 800 °C, 900 °C and 1000 °C for 10 min (Fig. 1). The spectrum of FT-IR indicates the presence of OH in the starting powder and also in the prepared ceramics (Fig. 2). The band due to the stretching vibrations of OH ion appears at 3571 cm^{-1} [17]. The amount of OH ion in HA ceramics sintered by SPS decreased with increasing temperature of sintering.

According to FT-IR and TG-DTA, the HA ceramics prepared at 800 °C was OH fully containing hydroxyapatite and the ceramics prepared at 900 °C was oxyhydroxyapatite, $Ca_{10}(PO_4)_6(OH)_{1.2}O_{0.4}\square_{0.4}$, where $\square$ is a neutral vacancy in the OH site.

Whereas in the case of normal sintering in air, densification started at about 900 °C [18-20], Nakahira et al. reported that dense HA ceramics was obtained at above 700 °C using SPS [21]. In this study, transparent HA ceramics were obtained by SPS at 900 °C and 1000 °C for 10 min (Fig. 3). These results proved that SPS is a potential method for fabricating highly densed HA ceramics at much lower temperature [22-23] like hot-pressing (HP) and hot isostatic pressing (HIP) [24-28]. According to the SPM observation, the ceramics prepared at 800 °C had a few pores. The average grain size of the ceramics sintered at 900 °C was around 0.2 μm. There were almost no pores in the ceramics.

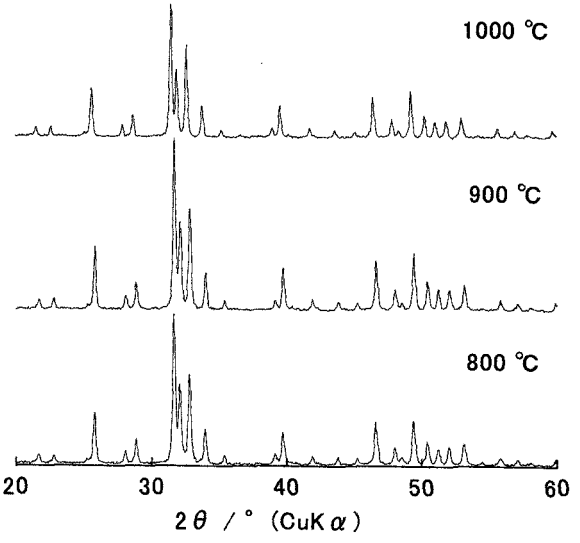

Fig. 1 XRD patterns of the HA ceramics prepared by SPS at 800 °C, 900 °C and 1000 °C.

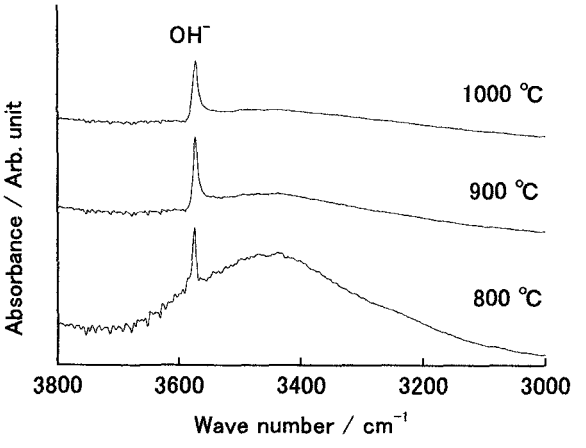

Fig. 2 IR spectra of HA ceramics prepared by SPS at 800 °C, 900 °C and 1000 °C.

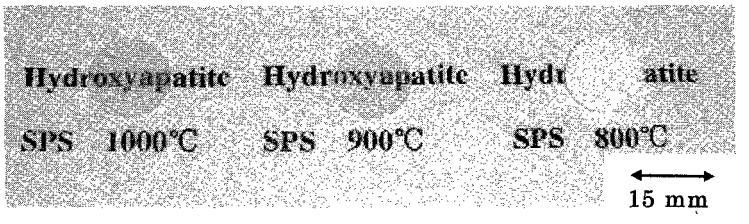

Fig. 3 OH-controlled HA ceramics prepared by SPS at 800 °C, 900 °C and 1000 °C.

3.2 Transparent β-TCP

No phases other than β-TCP were revealed by XRD in the starting sample and the samples after sintering by SPS at 800 °C, 900 °C and 1000 °C for 10 min (Fig. 4).

In the sintering process by SPS, the densification started at about 800 °C, and then proceeded with increasing temperature to result in line shrinkage of about 40 % at 1000 °C, which means the end of densification (Fig. 5). The β-TCP ceramics sintered by SPS at 800 °C, 900 °C and 1000 °C showed about 70 %, 95 % and over 99 % of a relative density. In the comparison with normal sintering [29-31], the SPS processing lowered the densification temperature as much as 200 °C.

In particular, a sintering period is quite short time. Transparent β-TCP ceramics were obtained by SPS at 1000 °C for 10 min (Fig. 6). Kondoh et al. reported that the transparent β-TCP ceramics were obtained by HIP'ing above 1000 °C and 100 MPa for 30 min [32]. This result proved that SPS is an available method for fabricating highly densified β-TCP ceramics.

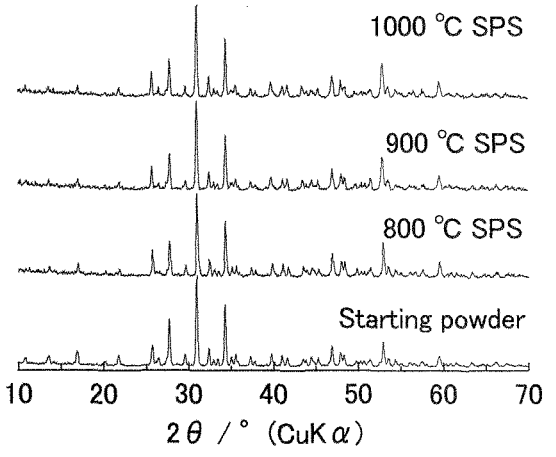

Fig.4 XRD patterns of the starting powder and β-TCP ceramics prepared by SPS at 800 °C, 900 °C and 1000 °C.

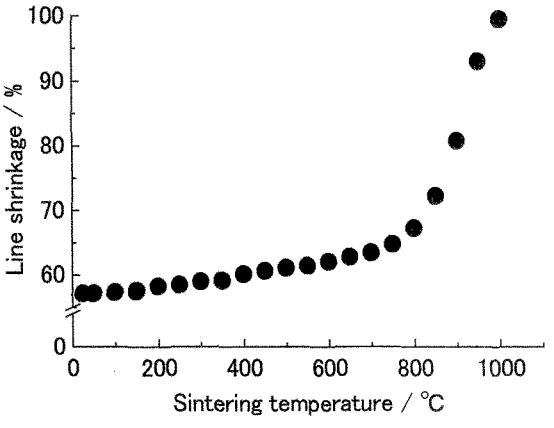

Fig. 5 Line shrinkage of β-TCP at the indicated temperatures by SPS.

According to the SPM observation, the β-TCP ceramics prepared at 800 °C had a few pores of about 0.1 μm in size. The SPM photograph of transparent β-TCP ceramics prepared at 1000 °C after etching is shown in Fig. 7. Average grain size of the β-TCP ceramics sintered at 1000 °C was around 1.5 μm. There were almost no pores in the transparent β-TCP ceramics.

4. SUMMARY

(1) OH controlled dense hydroxyapatite ceramics were prepared by spark plasma sintering at the temperatures from 800 °C to 1000 °C for 10 min. Transparent hydroxyapatite ceramics were prepared by SPS at 900 °C and 1000 °C. The amount of OH ion in the structure of hydroxyapatite was decreased with increasing temperature of sintering.

(2) Transparent β-TCP ceramics were obtained by SPS at 1000 °C for 10 min. The average grain size of the ceramics sintered at 1000 °C was around 1.5 μm.

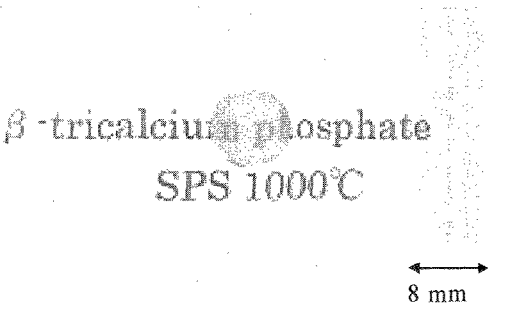

Fig. 6 β-TCP ceramics prepared by SPS at 1000 °C

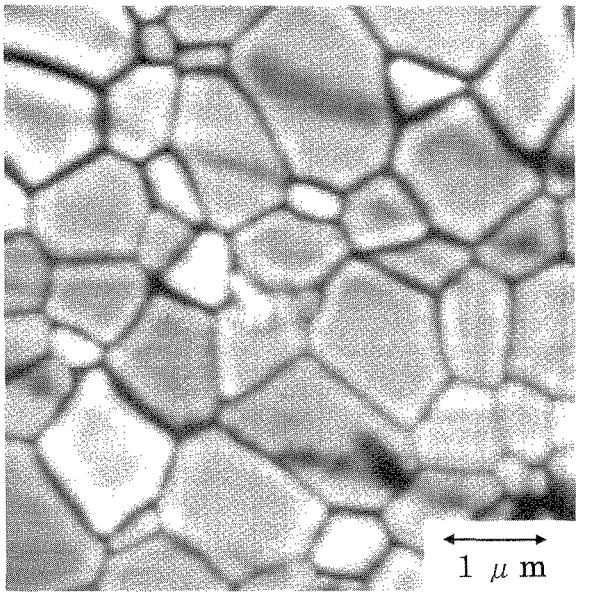

Fig. 7 SPM photograph of transparent β-TCP ceramics prepared by SPS at 1000 °C.

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