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OH-Designed Transparent Apatite Ceramics Prepared by Spark Plasma Sintering

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Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is one of the most interesting substance as biomaterials, column materials for chromatography, sensors and so on. It has been already suggested that the amount of OH in the structure of HA is closely related to the biocompatibility, the ability for bone formation and the ionic conductivity. Thus, OH-control in HA structure is necessary for the material designing. In this study, OH-controlled apatite ceramics were prepared by spark plasma sintering at the temperatures from 800 ℃ to 1100 ℃. The apatite ceramics prepared at 900 ℃ and 1000 ℃ showed transparency.

Key words: hydroxyapatite, sintering, spark plasma sintering, transparent, fine structure

1. INTRODUCTION

Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$: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 [1-4]. 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 [5]. 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 in HA was controllable by the control of heating conditions [6]. In this study, OH-controlled HA ceramics were prepared by spark plasma sintering, under the controlled sintering conditions.

2. EXPERIMENTAL PROCEDURE

2.1 Sintering Process

Fine powder of HA (High-purity grade Ube Materials, Japan) was used as the starting material. This powder of about 1g was poured into the graphite mold (inner diameter 15 mm), and then sintered by spark plasma sintering method (SPS: Dr Sinter-511S, Sumitomo Coal Mining, Kanagawa, Japan). The temperatures 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 10 MPa, and then they were heated at 800 ℃, 900 ℃ and 1000 ℃ for 10 min with the heating rate of 25 ℃·min^{-1}.

2.2 Characterization

The chemical composition of HA was analyzed by inductively coupled plasma spectrometer (ICP-MS: Seiko Inst., SPQ 9000S, Japan). The starting powder and the obtained ceramics were identified by powder X-ray diffractometer with graphite-monochromatized CuKα radiation, operated at 40 kV and 20 mA (XRD; Geiger flex 2027, Rigaku, Japan). The ceramics was polished with using a 4000-grid SiC and then polished finely with using a paste containing Al_2O_3 fine particles smaller than 0.5 μm in size. The hardness of samples was evaluated by an indentation method using a Vickers hardness tester (Model AVK-A II, Akashi, Japan) at the load of 300 gf for 10 s. After etching in 0.2 mol lactic acid solution for 50 s [7], the surface of ceramics was observed by using field emission scanning microscopy (FE-SEM; JSM 820, JEOL, Japan). The amount of OH ion in the ceramics was analyzed quantitatively by infrared spectroscopy (FT-IR; Spectrum 2000, Perkin Elmer). Thermogravimetry and differential thermal analysis (TG-DTA; TG-DTA32, Seiko Instruments Inc.

Japan) was executed under the following condition: 10 mg of samples, α-Al_2O_3 reference, and a heating rate of 10 ℃·min^{-1} from room temperature to 1200 ℃.

3. RESULTS AND DISCUSSION

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 μm by TEM observation (Fig. 1). The size and shape of particles were relatively homogeneous.

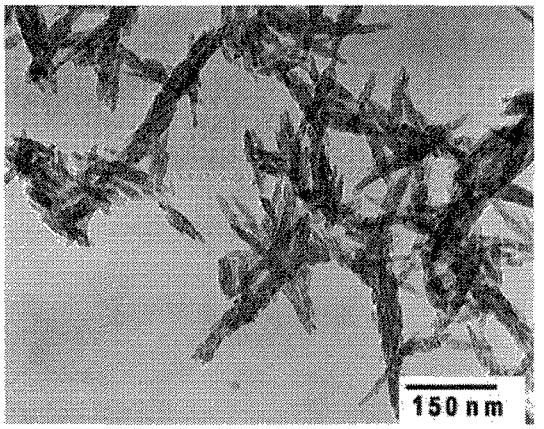

Fig.1 TEM photograph of starting powder of HA.

No phases other than HA were revealed by XRD for the starting samples and samples after sintering by SPS at 800 ℃, 900 ℃ and 1000 ℃ for 10 min (Fig. 2). The spectrum of FT-IR indicates the presence of OH^- in the starting powder and also in the prepared ceramics (Fig. 3). The band due to the stretching vibrations of OH ion appears at 3571cm^{-1} [8]. 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 ℃ was OH fully containing hydroxyapatite and the ceramics prepared at 900℃ was oxyhydroxyapatite $(Ca_{10}(PO_4)_6(OH)_{1.2}O_{0.4}\square_{0.4}$, where □ is a neutral vacancy in the OH site).

In the sintering process by SPS, the densification started at about 630 ℃, and then proceeded with increasing temperature to result in line shrinkage of about 2.2 mm at 900 ℃ (Fig. 4), which means the end of densification. The HA ceramics sintered by SPS at 800 ℃ showed about 90 % relative density, and the

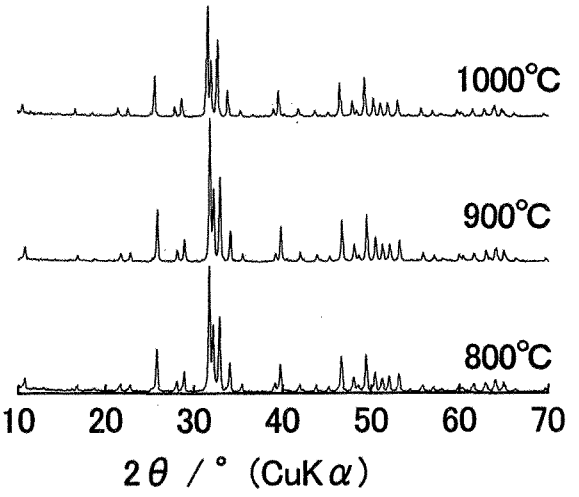

Fig.2 Patterns of XRD of ceramics prepared by SPS at 800 ℃, 900 ℃ and 1000 ℃.

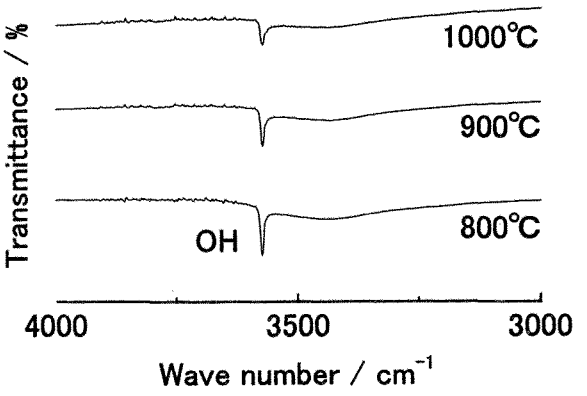

Fig.3 IR spectra of HA ceramics prepared by SPS at 800 ℃, 900 ℃ and 1000 ℃.

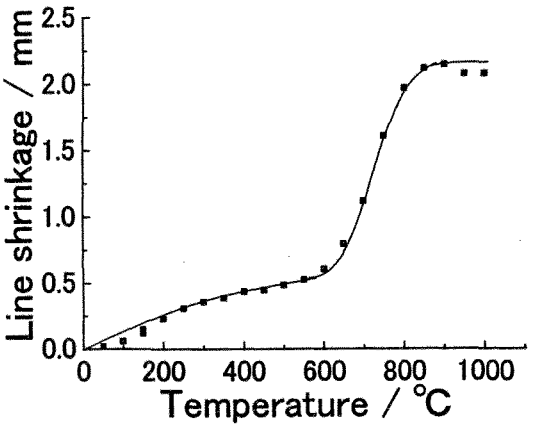

Fig.4 Line shrinkage of HA at the indicated temperatures by SPS.

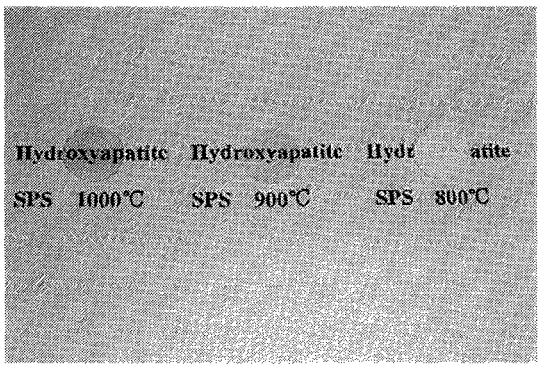

Fig.5 OH-controlled HA ceramics prepared by SPS at 800 ℃, 900 ℃ and 1000 ℃.

ceramics sintered at 900 ℃ and 1000 ℃ showed over 99 % relative density. Whereas in the case of normal sintering in air, densification started at about 900 ℃ [9]. 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) [9-13]. In particular, sintering period is quite short time. Transparent HA ceramics were obtained by SPS at 900 ℃ and 1000 ℃ for 10 min (Fig. 5).

According to the FE-SEM observation, the ceramics prepared at 800 ℃ had a few pores of about 0.1 μm in size. The FE-SEM photograph of transparent ceramics prepared at 900 ℃ after etching is shown in Fig.6. Average grain size of the ceramics sintered at 900 ℃ were around 0.15 μm. There were almost no pores in the ceramics.

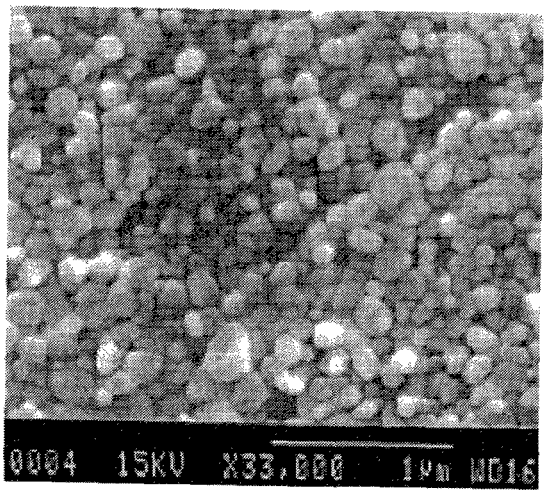

Fig.6 FE-SEM photograph of transparent HA ceramics prepared by SPS at 900℃.

4. SUMMARY

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

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