Densification Behavior of Various Hydroxyapatite Powders by Spark Plasma Sintering

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Hydroxyapatite(HA), $Ca_{10}(PO_4)_6(OH)_2$, is one of the most biocompatible materials with human bones. HA is a promising bone substitute material for clinical application because of clinical stability *in vivo*. Fine powder of HA were heated at 900°C for 1 h and at 1000°C for 6 h in air. The first objective of this study is to reveal the effect of plastic flow on densification behavior by spark plasma sintering (SPS) from various preheated HA powders. From the isothermal shrinkage behavior, we concluded that the plastic flow in later stage does not depend on the preheating temperature. The second objective of this study is to prepare graduated HA ceramics for artificial bone by SPS. These heating powders (0.25 g) were vertically laminated into the graphite mold and then sintered by SPS at the temperatures from 800°C for 10 min with a heating rate of 25 K min^{-1}. The ceramics prepared by SPS had pores of about 0.1 μm after heated at 1000°C for 6 h. There were no pores in HA ceramics prepared by SPS before heated at 900°C for 1h.
Key words: hydroxyapatite, spark plasma sintering, FGM, densification behavior

1. INTRODUCTION

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, has the attractive feature of biocompatibility for the human hard tissue, and thus many clinical applications of HA were carried out as artificial bones and teeth roots [1-4].

An innovative powder densification technology known as spark plasma sintering (SPS) has been developed in recent years. By applying high temperature spark plasma generated momentarily, the SPS is able to sinter at low temperature and in a short period [5-6]. SPS can be an effective method to prepare HA ceramics [7-8]. Ioku et al. reported that transparent HA ceramics and β-tricalcium phosphate were prepared by SPS at 900°C and 1000°C for 10 min [9-14]. These reports were proved that SPS is a potential method for fabricating highly densified HA ceramics at much lower temperature like hot-pressing and hot isostatic pressing [15-19].

The first objective of this study is to reveal the effects of plastic flow on SPS from various preheated HA powders.

On the other hand, a functionally graded material (FGM) is a composite material consisting of two or more phases in which the volume fractions of the constituents change so that the composition, microstructure and properties vary gradually along one direction. Designing FGM allows manipulation of many material properties or new functions. These allow obtaining a change in properties in the direction parallel to the imposed gradient. Changes in mechanical properties, optical properties, electrical properties thermal conductivity, hardness and brittleness can be achieved.

The SPS process is expected to find increasing usage in the fabrication of FGM, intermetallic compounds, fiber reinforced ceramics, metal matrix composites, nanocrystalline materials, which are difficult in sintering by common methods. As a rapid consolidation technique, the SPS process has many advantages on fabrication of FGM. Therefore, the second objective of this study is to prepare graduated HA ceramics for artificial bone 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. HA powder were heated at 900°C for 1 h and at 1000°C for 6 h in air. These powders ware used normal sintering and SPS.

These preheated powders (0.25 g) were vertically laminated, and then normally sintered at 900°C for 3 h in air.

These preheated powders (about 0.5 g) were poured into the graphite mold (inner diameter 10 mm), and sintered by SPS method (SPS: Dr Sinter-511S, Sumitomo Coal Mining, Co. Ltd., Japan) as shown in 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 uniaxialy under 30 MPa, and then they were heated at 800°C for 10 min with a heating rate of 25 K · min^{-1}.

2.2 Characterization

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; MXP3, MAC Science Co. Ltd., Japan). The obtained ceramics were polished with using a 4000-grid SiC. Density measurements based on Archimedes' principle were conducted. Theoretical

density of HA was assumed to be 3.16 g·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, α -Al$_2$O$_3$ reference, and a heating rate of 10 K · min^{-1} from room temperature to 800 $^\circ$C. The compressive strength of porous ceramics was measured by mechanical testing machine (Universal Testing Machine; AG-M1 50kN, Shimadzu Corporation, Japan).
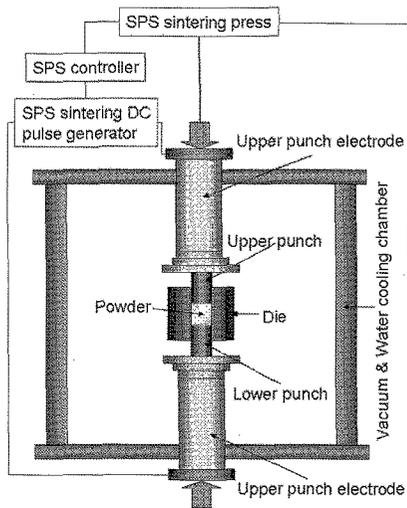
Fig. 1 Schematic representation of spark plasma sintering system.

3. RESULTS AND DISCUSSION

From the densification behavior of HA powders heated at 900°C for 1h and at 1000°C for 6 h during sintering by SPS, ln (1 - D) were plotted against sintering period according to the Murray's equations [20-21] on SPS at 800°C.

$$\ln\left(1-D\right) = -\frac{3\sigma}{4\eta}\ \ t + C \quad (1)$$

where D is relative density, σ is applied stress, n is viscosity coefficient, t is hold time and C is constant. In case the plot of line shrinkage on isothermal sintering fits on Murray's equations, dominant sintering mechanism is plastic flow.

In analysis of densification process of HA on SPS at 800°C under 30 MPa after heated at 900°C for 1h and at 1000°C for 6 h (Fig. 2), the liner shrinkage was nearly straight in the later stage. As the liner shrinkage fitted on . Murray's equations, dominant sintering mechanism of SPS was plastic flow of densification. Ioku et al. reported that in analysis of plastic flow of HA from fine crystal powder on SPS at 800 $^\circ$C under 60 MPa, dominant sintering mechanism of SPS was plastic flow [22]. In the present study, with various size of HA powders, densification behavior in SPS at 800°C were investigated. There was no difference in plastic flow on SPS at 800°C between preheated at 900°C for 1 h and at 1000°C for 6 h. In early stage, the slopes were different. Then, rearrangement of particle was different between

these two liner shrinkages.

No other phase except for HA were revealed by XRD for the samples after normal heating at 900°C for 1 h, the samples after normal heating at 1000°C for 6 h and samples after sintering by SPS at 800°C for 10 min (No figure).
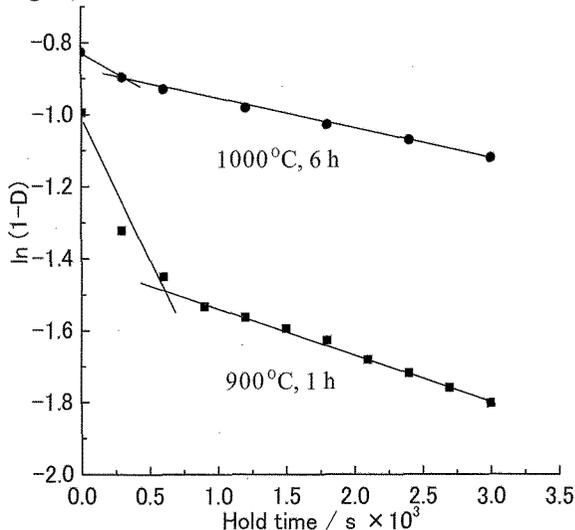

Fig. 2 Isothermal shrinkage behavior of preheated HA powder sintered at 800°C by SPS method.
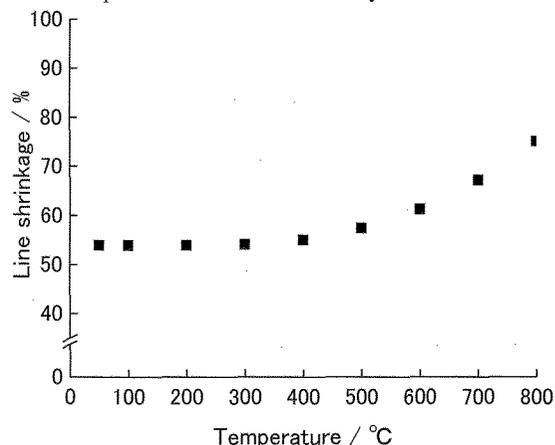

Fig. 3 Relative density of preheated HA at the indicated temperatures by SPS method.

Relative density of heated HA at the indicated temperatures by SPS method is shown in Fig. 3. The densification in this study started at about 600°C. Whereas densification started at about 900°C in the case of normal sintering in air [23], the densification by SPS method started at about 600°C [12].

The obtained ceramics were cut into two and the fracture surface was polished with using a 4000-grid SiC. According to the SEM observation result in Fig. 4, the ceramics prepared by normal sintering at 800°C had a pores of about 1.0 μm in part of HA after heating 900°C at 1 h and about 5.0 μm in part of HA after heating at 1000°C for 6 h. Average grain size of the ceramics in part of HA after heating at 900°C for 1 h and in part of HA after heating at 1000°C for 6 h were 2.0 μm, 10.0 μm, respectively. The ceramics prepared by SPS at 800

°C had pores of about 2.0 μm in part of HA before heating at 1000°C for 6 h. There were no pores in HA ceramics prepared by SPS at 800°C after heated at 900 °C for 1h. Average grain size of the HA ceramics prepared by SPS at 800°C in part of HA after heating at 900°C for 1 h and in part of HA after heating at 1000°C for 6 h were 1.5 μm, 5.0 μm respectively.

The measured compressive strength of HA prepared by SPS at 800°C for 10 min was high as 170 MPa with a porosity of 30%.

All these results suggested that there was possibility of fabrication of graduated HA ceramics for artificial bones.
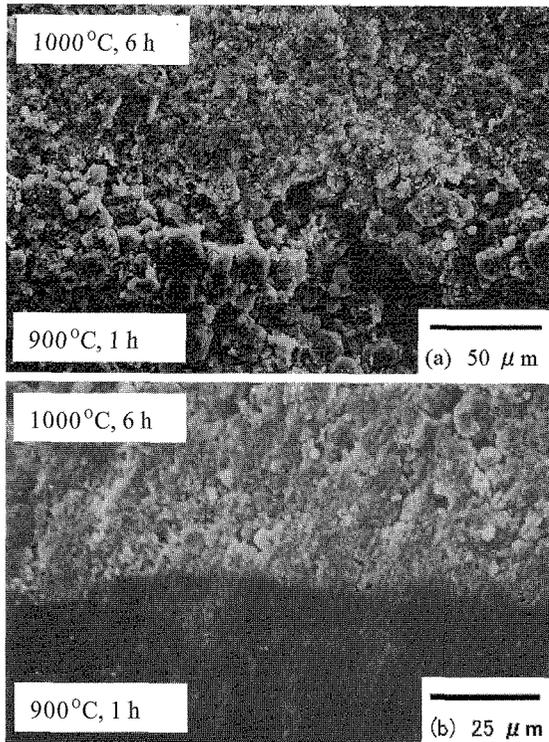

Fig. 4 SEM photographs of HA ceramics prepared by a) normal sintering at 900°C for 3 h. b) SPS at 800 °C for 10 min. In each photograph, the upper part and bottom part of photograph indicate preheating at 1000°C for 6 h and preheating at 900°C for 1 h, respectively.

4. SUMMARY

(1) Dominant sintering mechanism of SPS was plastic flow and rearrangement of particle was different.

(2) Graduated hydroxyapatite ceramics were prepared by spark plasma sintering at the temperatures from 800 °C for 10 min.

5. Acknowledgments

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