Transparent β -Tricalcium Phosphate Ceramics Prepared by Spark Plasma Sintering

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放電プラズマ焼結による β -リン酸三カルシウム透明体の作製

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β -tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$, β -TCP) is known to be biocompatible and osteoconductive. In the present study, β -TCP ceramics were prepared by the spark plasma sintering (SPS) technique at temperatures ranging from 800 to 1000°C at a pressure of 60 MPa for 10 min at a heating rate of 25°C/min. No phases other than β -TCP were detected in the samples sintered at 800, 900 and 1000°C by X-ray diffractometry. The relative densities of the β -TCP ceramics sintered at 800, 900 and 1000°C were 70, 95 and more than 99%, respectively. Transparent β -TCP ceramics were obtained at 1000°C for 10 min. From the results obtained by scanning probe microscopy, the ceramics prepared at 800 and 900°C were found to have a few pores. The transparent ceramics had an average grain size of 1.5 μm and seemed to be pore-free.

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Key-words : β -tricalcium phosphate, Sintering, Spark plasma sintering, Transparent ceramics, Microstructure

1. Introduction

β -tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$, β -TCP) is known to be biocompatible and osteoconductive.^{1)–6)} The spark plasma sintering (SPS) method is quite effective for producing dense ceramics of calcium phosphates.^{7),8)} In the present study, β -TCP ceramics were prepared by SPS at temperatures ranging from 800 to 1000°C at a uniaxial pressure of 60 MPa for 10 min with a heating rate of 25°C/min.

A fine powder of β -TCP (Taihei Chemical Industrial Co., Ltd.) was used as the starting material. This powder of 0.5 g was placed in a graphite mold (8 mm inner diameter), and then sintered by SPS (Dr Sinter-511S, Sumitomo Coal Mining Co., Ltd., Kanagawa). The temperature of the samples during sintering was measured using a thermocouple of Rh/Pt–Pt, inserted into the wall of the graphite mold.

2. Experimental procedures

The starting powder and the obtained ceramics were identified using an X-ray powder diffractometer with graphite-monochromatized Cu K α radiation, at 40 kV and 20 mA (Geiger flex 2027, Rigaku). The ceramics were polished with 4000-grid SiC and further polished with a paste containing fine α - Al_2O_3 particles smaller than 0.5 μm . The Vickers hardness of the samples was measured at a load of 3 N for 10 s (AVK-AII, Akashi Seisakusho, Co., Ltd.). The density of the sintered specimens was estimated by the Archimedes immersion technique. After thermal etching at 10°C below the sintering temperature for 10 min, the surface of the ceramics was observed by scanning probe microscopy (SPM, Nanopics 2100, Seiko Instruments). SPM was operated with a Si cantilever at a resolution of 0.3 nm. The detected tip amplitude was tuned at 1.0 V.

3. Results and discussion

From the chemical analysis results presented by Taihei Chemical Industrial Co., Ltd., the β -TCP used contained little

Fig. 1. XRD patterns of starting material and β -TCP ceramics prepared by SPS at 800, 900 and 1000°C.

impurities: Cl, <20 mass ppm; SO_4 , <50 mass ppm; Fe, <10 mass ppm; As, <1 mass ppm; Mg, <50 mass ppm; and Mn, <20 mass ppm. The XRD patterns of the starting material and the samples prepared by SPS at 800, 900 and 1000°C for 10 min (Fig. 1) revealed no second phase other than β -TCP. Therefore, the starting material of β -TCP has a stoichiometric Ca/P molar ratio of 1.50. In the SPS process, densification was started at 800°C, and then proceeded at elevated temperatures. The resultant linear shrinkage was 40% at 1000°C, which denotes the end of densification (Fig. 2). The β -TCP ceramics prepared by SPS at 800, 900 and 1000°C had relative densities of 70, 95 and more than 99% and Vickers hardness of 2.5, 4.8 and 5.0 GPa, respectively (Fig. 3). The densification temperature of the SPS process became 200°C lower than that of the normal sintering process.^{9)–11)} In particular, the sintering was completed within a short time. Transparent β -TCP ceramics were obtained by SPS at 1000°C for 10 min (Fig. 4). Kondoh et al.¹²⁾ reported that the transparent β -TCP ceramics were obtained by HIP'ing above 1000°C at a pressure of 100 MPa for 30 min. The present result demonstrated that SPS is

Fig. 2. Relative density of β -TCP ceramics prepared by SPS at indicated temperatures.

Fig. 3. Relative density and Vickers hardness of β -TCP ceramics prepared by SPS at 800, 900 and 1000°C.

Fig. 4. β -TCP ceramics prepared by SPS at 900 and 1000°C.

an available method for fabricating highly densified β -TCP ceramics. From SPM observations, the ceramics prepared at 800°C had a few pores of 0.1 μm diameter. The SPM image of the transparent ceramics prepared at 1000°C after the etching is shown in Fig. 5. The average grain sizes of the ceramics sintered at 800, 900 and 1000°C were 0.8, 1.0 and 1.5 μm , respectively, and there was almost no pore in the transparent ceramics. The transparent β -TCP ceramics prepared in this study must be used in directly observing cultured cells.

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Fig. 5. SPM image of transparent β -TCP ceramics prepared by SPS at 1000°C.

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