Hydrothermal Sintering under Mild Temperature Conditions: Preparation of Calcium-deficient Hydroxyapatite Compacts

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Calcium-deficient hydroxyapatite (CDHA) prepared by the coprecipitation method was solidified by the hydrothermal hot-pressing technique, and compacts of CDHA with high bulk density beyond 80 % were obtained at 200 °C. Each reaction parameter, *viz.* reaction temperature, pressure, and time, was systematically changed from the standard conditions to investigate its effects on density, Vickers hardness, and Ca/P ratio of the compacts obtained. The reaction temperature and pressure had a large effect on densification, but not the reaction time because the densification proceeds in a short time. The densification by hydrothermal hot-pressing involved dissolution and precipitation of the starting CDHA powder, so that the Ca/P ratio changed from 1.52 of the starting powders to 1.61 of the compact obtained by hydrothermal hot-pressing at 200 °C and 35 MPa for 24 h with the addition of 10 wt.-% water.

Key words: Calcium-deficient Hydroxyapatite, Hydrothermal Hot-Pressing, Hydrothermal Sintering, Low-temperature Densification, Ca/P Ratio

Introduction

The hydrothermal hot-pressing technique has been developed to prepare densified compacts with high mechanical strength by continuous compression of powders under hydrothermal conditions at low temperatures [1]. The compression accelerates the densification of the powders, and the hydrothermal reaction causes linkage of the powder particles. This technique has been used to prepare many kinds of compacts from glasses [2, 3], silica gel [4], low quartz [5], zeolite [6, 7], mesoporous silica [8, 9], zirconia [10, 11], anatase [12, 13], hydroxyapatite [14 – 20], calcite [21 – 25], and others. When the starting materials have sufficient solubility or react with other materials under hydrothermal conditions, the compacts are obtained upon the addition of pure water by a dissolution and precipitation mechanism. When the starting materials are not active under hydrothermal conditions, mineralizers such as aqueous NaOH solution are used to get the compacts. The hydrothermal hot pressing technique is also useful for solidification of industrial wastes such as glass wastes [3, 26], slug [27], incinerated ash [28], concrete wastes [29], and radioactive wastes [30 – 35].

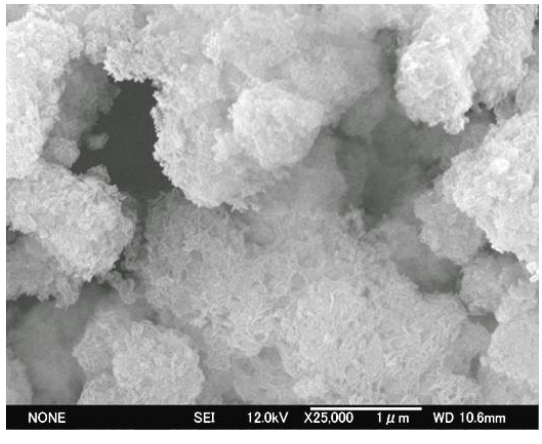

Fig. 1. FE-SEM image of a CDHA powder prepared by the coprecipitation method.

The hydrothermal hot pressing technique is considered as pressure sintering with the presence of a liquid phase. It has been clarified that the densification of

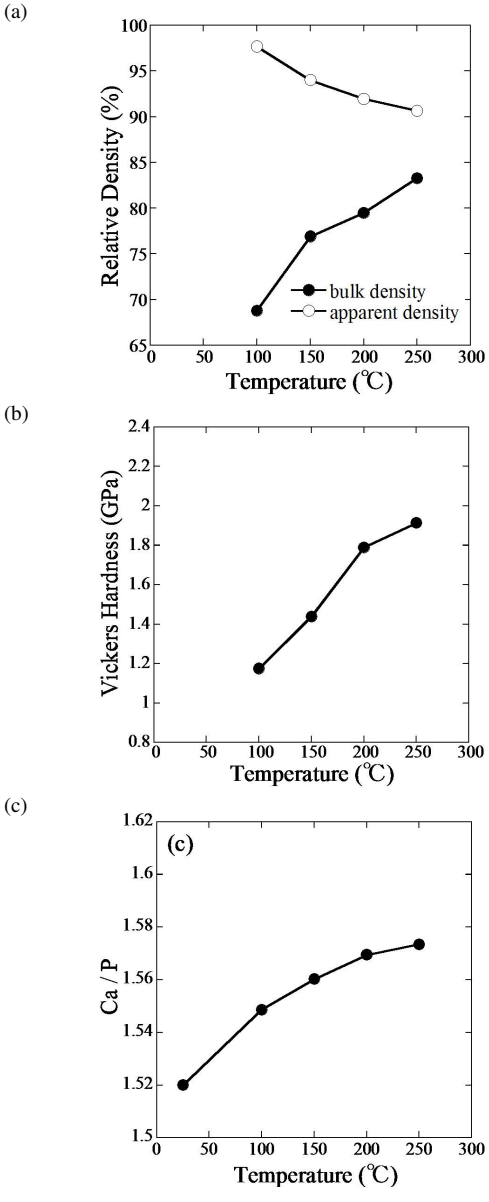

Fig. 2. Effects of the reaction temperature on the relative density (a), Vickers hardness (b), and the Ca/P ratio (c).

glass powders during hydrothermal hot pressing proceeds by a viscous flow mechanism [2]. This technique is useful for the solidification of powders which decompose by calcination in air at high temperatures and/or are stable under hydrothermal conditions. Examples are calcite, anatase, hydroxides, and others.

Hydroxyapatite (HA) is a major inorganic component of bone and teeth, and has been applied in many kinds of biomaterials, including bone substitutes. The

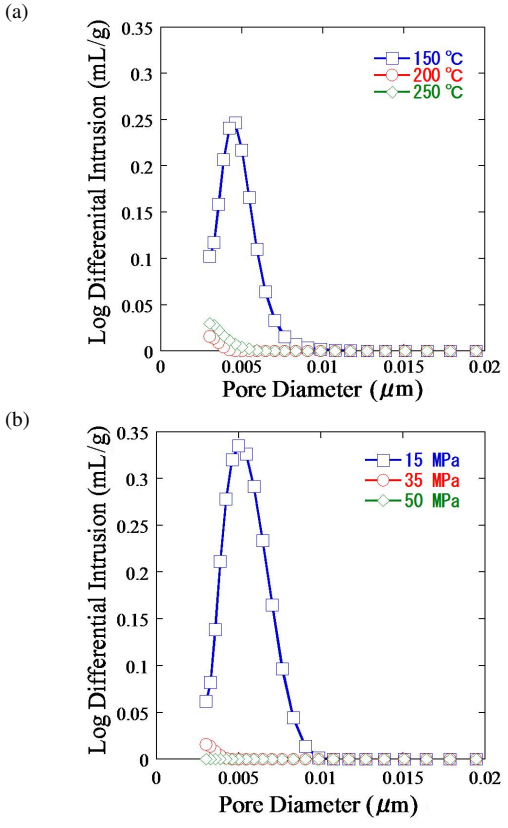

Fig. 3. Pore diameter distribution of the compacts prepared at various temperatures (a) and pressures (b).

molar ratio Ca/P of HAs in the bone was reported to be lower than the stoichiometric Ca/P ratio of pure HA (1.67) [36 – 38]. Thus, it is expected that calcium-deficient hydroxyapatite (CDHA) has higher osteoconductive and osteoinductive properties than stoichiometric HA. It is possible to densify HA by sintering at high temperatures in air [39, 40], but the calcination at high temperatures causes growth of HA particles and a release of hydroxyl groups. Furthermore, CDHAs decompose to HA and tricalcium phosphate at high temperatures [39 – 42]. It is difficult to prepare CDHA compacts by sintering at high temperatures. In work described in this paper, we applied the hydrothermal hot pressing technique to prepare compacts consisting of low-crystallinity CDHA.

Results and Discussion

An FE-SEM image and XRD diffraction patterns of coprecipitated CDHA powders are shown in Figs. 1 and 5, respectively. The powders are low-crystallinity

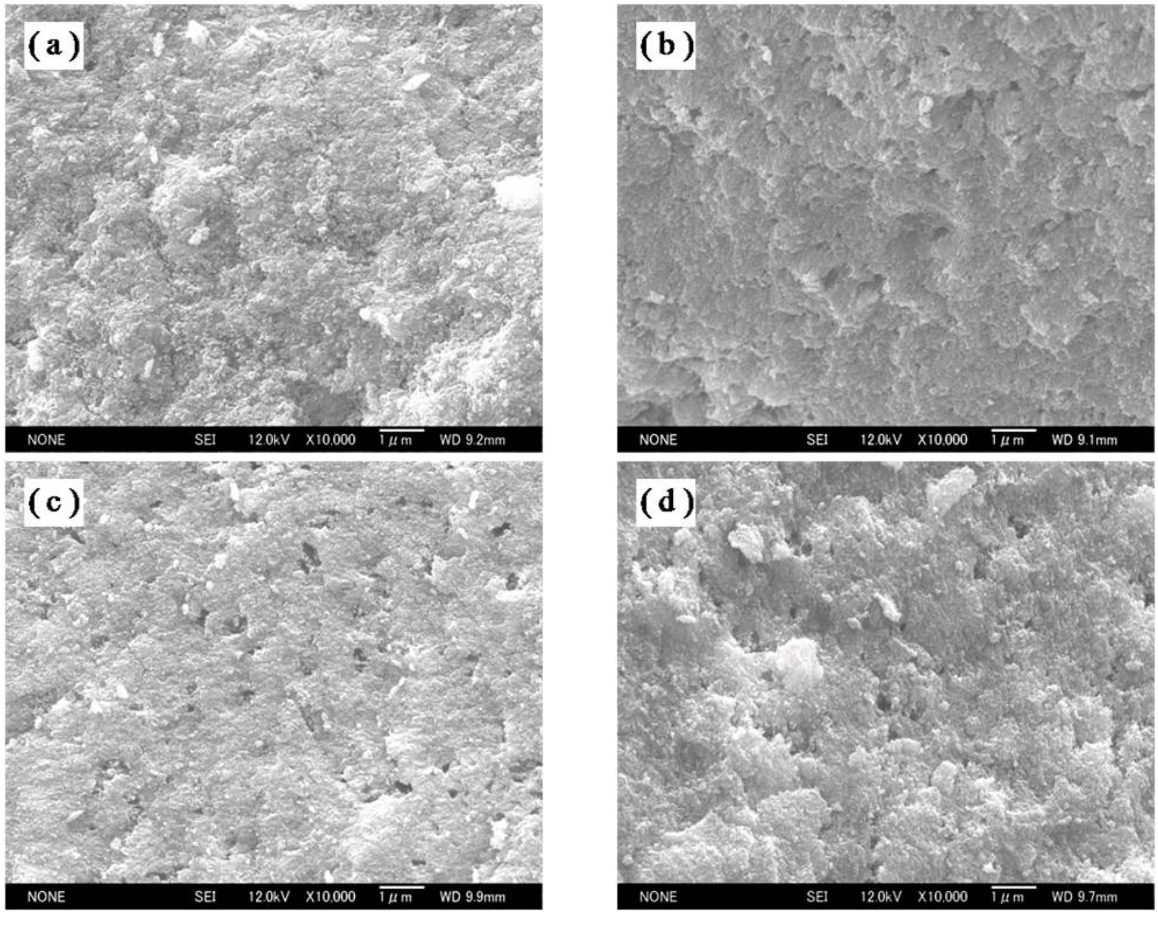

Fig. 4. FE-SEM fracture surface images of the compacts prepared at 100 °C (a), 150 °C (b), 200 °C (c), and 250 °C (d).

HA without any impurity phases consisting of lightly agglomerated fine flakes less than 100 nm in size. It has been confirmed by chemical analysis that the powder was calcium-deficient with a Ca/P ratio of 1.52.

For densification by hydrothermal hot pressing, three reaction parameters, *viz.* reaction temperature, pressure, and time, were systematically changed from the standard conditions, 200 °C, 35 MPa, and 6 h, respectively, and the effects of each parameter on relative density, Vickers hardness, and Ca/P ratio of the compacts were examined.

Effect of the reaction temperature

Bulk density and Vickers hardness remarkably increased with the increase in reaction temperature (Fig. 2a, b), which suggests that the densification proceeded at high temperatures. The apparent density decreased with the increase in reaction temperature. In other words, the compacts obtained at low temperatures had a large amount of open pores. The open pore volume ratio against the total pore volume of the compacts obtained at 100 °C was 97 % and decreased to 53 % for the compact obtained at 250 °C. The pore diameter distribution measured by the mercury intrusion method showed open pores larger than 20 nm were not observed in any compacts, and that the compact prepared at 150 °C had open pores with 5 nm in diameter, but the compacts prepared at temperatures beyond 200 °C had only a small amount of open pores (Fig. 3a). Fracture surfaces are shown in Fig. 4. The starting particles were well compacted at 100 °C, and no pores were observed at this magnification. However, pores with over 100 nm in size were observed in fracture surfaces, when the reaction temperature was increased. The observed pores thus must be closed.

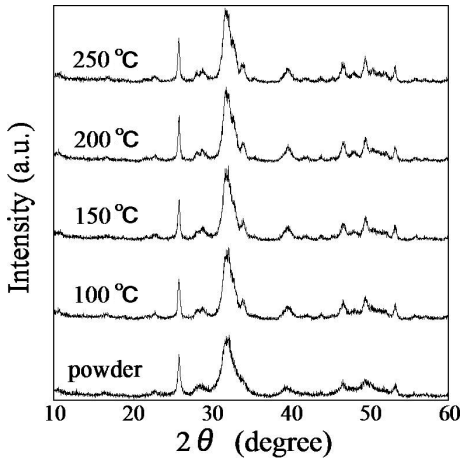

Fig. 5. XRD patterns (CuK_α radiation) of the compacts prepared at different temperatures.

The Ca/P ratio of the compacts increased with the increase in reaction temperature, which suggests that the hydrothermal reaction proceeded during hydrothermal hot pressing. This result was supported by the XRD diffraction patterns (Fig. 5) which showed that the crystallinity of the HA phase in the compacts was slightly increased by hydrothermal treatment in comparison with that of the starting powder. It is to be noted that even the HA phase of the compacts obtained at 250 ℃ had low crystallinity. It has been reported that the dissolved amount of CDHA in water at 37 ℃ increases with a decreasing Ca/P ratio [43]. In our study, the CDHA powder with a Ca/P ratio of 1.52 was hydrothermally treated in a very small amount of water (10 wt.-%). The starting powder might be dissolved in water very quickly under hydrothermal conditions to produce high supersaturation for recrystallization of HA. The Ca/P ratio of the compacts was determined after the powders were soaked in water to remove soluble materials formed by hydrothermal hot pressing. Water was acidified by soaking the powders, which suggests that CDHA underwent non-stoichiometric dissolution [44] to release a higher amount of phosphate in comparison with calcium. This result agreed with a previous report which has shown that the phosphate content in water was higher than the calcium content when CDHA was dissolved in water at 37 ℃ [43]. Non-stoichiometric dissolution of CDHA in a small amount of water by hydrothermal hot pressing might cause a drastic change of the composition of the solution and lead to precipitation of HA with a different composition from the solution. HA with a higher

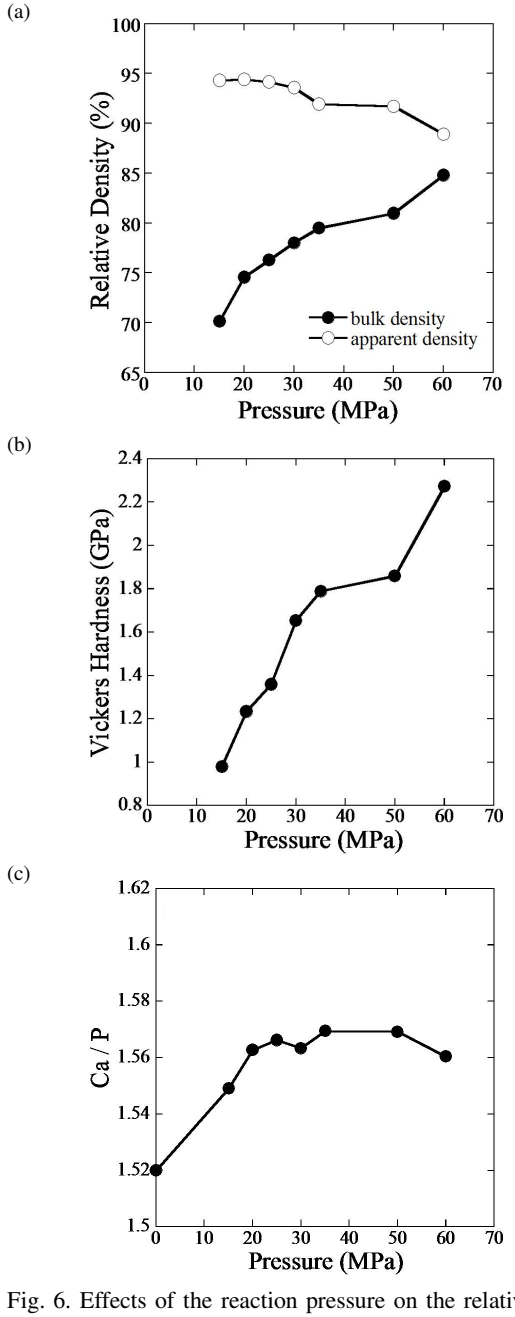

Fig. 6. Effects of the reaction pressure on the relative density (a), Vickers hardness (b), and the Ca/P ratio (c).

Ca/P ratio than that of the starting CDHA may crystallize during hydrothermal hot pressing to leave a large amount of phosphate in solution. The densification by hydrothermal hot pressing therefore involves dissolution and precipitation of the starting CDHA powder.

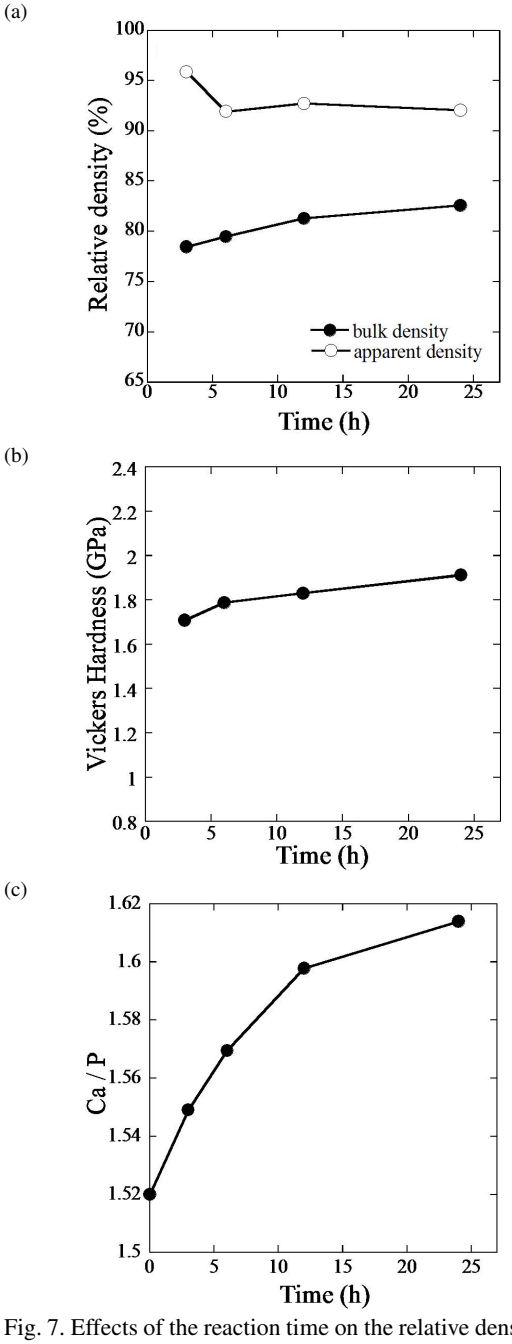

Fig. 7. Effects of the reaction time on the relative density (a), Vickers hardness (b), and the Ca/P ratio (c).

Effect of the reaction pressure

When the reaction pressure was increased, bulk density and Vickers hardness of the compacts were increased (Fig. 6a, b), like through the effect of the reaction temperature. Fine pores were detected only in the compacts prepared at low pressure (15 MPa), as shown in Fig. 3b. High reaction pressure (60 MPa) gave compacts with higher Vickers hardness (2.27 GPa) in comparison with that obtained at 250 °C (1.91 GPa), though their bulk and apparent density were the same as 84 % and 90 %, respectively. The fracture surface observation (not shown) revealed that the number and size of closed pores were decreased in the compacts obtained at 60 MPa compared with that prepared at 250 °C, which explains the increase in Vickers hardness. The Ca/P ratio did not change with the reaction pressure and was in the range of 1.55 and 1.57 (Fig. 6c). The reaction pressure thus has little effect on the hydrothermal reaction.

Effect of the reaction time

The reaction time had little effect on density and Vickers hardness (Fig. 7a, b). This result suggests that the densification proceeds within a short time. On the other hand, the reaction time had a large effect on the Ca/P ratio (Fig. 7c). The Ca/P ratio of the starting powder increased from 1.52 to 1.61 for the compact prepared by hydrothermal hot pressing for 24 h. This result has revealed that hydrothermal reactions proceeded even after the densification of the starting powder was completed by hydrothermal hot pressing.

Experimental Section

The starting materials were all purchased from Wako Pure Chem. Ind., Japan. The Ca-deficient HA powder was prepared by a coprecipitation method from equivalent amounts of aqueous solutions of 0.765 M $Ca(NO_3)_2$ and 0.5 M $(NH_4)_2HPO_4$. The pH value was adjusted to 9.5 by aqueous ammonia only for the aqueous solution of $(NH_4)_2HPO_4$. The precipitate was washed with diluted aqueous ammonia and water, and subjected to freeze drying.

The powder (5.0 g) was mixed with pure water (0.5 mL), transferred to a cylindrical autoclave (2.0 cm inner diameter) for hydrothermal hot pressing, and uniaxially compressed at a desired pressure (15 – 50 MPa). The autoclave was heated to a temperature of 100 – 250 °C, and the temperature and pressure were kept constant for 3 – 48 h. After drying at 110 °C, the bulk density of the obtained compacts was measured from their weight and apparent volume, and the apparent density was measured by Archimedes' principle using water. The relative density was calculated against the density of stoichiometric HA (3.155 $g \cdot cm^{-3}$). The microhardness was measured by a Vickers hardness tester (MVK-EIII, Akashi Seisakusho, Japan), and the pore diameter distribution was measured by the mercury intrusion technique

(Auto Pore 9520, Shimadzu Co., Japan). Fracture surfaces of the compacts were observed by scanning electron microscopy (JSM-6500F, JEOL, Japan), and crystalline phases were identified by powder X-ray diffraction on a Rigaku RTP-300RC diffractometer operating at 40 kV and 100 mA using CuK_α radiation (1.54056 Å). The Ca/P ratio was determined by quantitative analysis using inductively-coupled plasma emission spectrometry (SPS7000A, Seico Electronics, Japan). Before the analysis, the compacts were crashed, washed with water, and then dissolved in nitric acid.

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