Densification and Superplasticity of Hydroxyapatite Ceramics

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Fabrication conditions for high-density and fine-grained hydroxyapatite \((\text{Ca}_n\text{(PO}_4)_6\text{OH})_2\); HAp) ceramic were examined; the tensile elongation of HAp ceramic during heating was measured in order to evaluate its possible superplastic behavior. The HAp compact was fired in air at a temperature between 1100 and 1200°C for 5 h. The relative density of HAp compact fired at 1100°C for 5 h showed a maximum (99.2%), whereas the average grain size was as small as 0.56 μm. The tensile elongation of this HAp specimen was tested at a temperature between 940 and 1100°C. The tensile elongations tested at 1050 and 1100°C attained 156 and 157%, respectively; the specimen tested at 1050°C contained a limited number of cavities, whereas the specimen tested at 1100°C was observed to have a large number of cavities.

Key-words : Hydroxyapatite, High density, Fine grains, Tensile elongation, Superplasticity

1. Introduction

Although the ceramics generally possess excellent heat-resistance and mechanical properties, the processing of ceramics is difficult, due to their low fracture toughness properties. Thus “near-net-shape” processing is required in order to fabricate the complex shaped ceramics with high degree of dimensional accuracy. A superplastic deformation is expected as a novel technique for processing such near-net-shaped ceramics.1,2 In order to achieve the superplastic deformation sufficient for the practical uses, the ceramics have to be extremely dense without any defects. In addition, the following conditions are required for the superplasticity: (i) the inhibition of grain growth (usually < 1 μm) and (ii) the control of strain rate (often close to \(10^{-4} \text{s}^{-1}\)).2,3 Owing to the strict control of these parameters, some of the present authors succeeded in achieving the tensile elongations of approximately 550% for alumina (\(\text{Al}_2\text{O}_3\))-10 vol% zirconia (\(\text{ZrO}_2\)),4 1000% for 0.3 vol% \(\text{Al}_2\text{O}_3\)-dispersed tetragonal \(\text{ZrO}_2\),5 2500% for 40\(\text{ZrO}_2\)(3Y)-30\(\text{MgAl}_2\text{O}_4\)-\(\text{Al}_2\text{O}_3\).6

A hydroxyapatite \((\text{Ca}_10\text{(PO}_4)_6\text{OH})_2\); HAp) ceramic, which is biocompatible with bone,7,8 is used for orthopaedic and dental implants.9,10 Although the block-type HAp ceramic is utilized as a restorative material for the skull,10 the processing of such HAp ceramics for the desired shape is a very important problem to solve. As described above, the excellent superplasticity of HAp ceramic may be realized when the HAp ceramic is composed of submicrometer-scaled grain sizes. The fabrication of full-density HAp ceramic with extremely small grains needs the utilization of easily-sinterable HAp powder with well dispersed and submicrometer-scaled primary particles and the strict control of sintering conditions. For example, the present authors have prepared the HAp powder by spray-pyrolysis technique, i.e., the spray-pyrolysis of the solution with Ca\((\text{NO}_3)_2\) and \(\text{(NH}_4)_2\text{HPO}_4\) in the hot zone of a furnace.31 By making use of the ultrafine HAp powder prepared through such spray pyrolysis (crystallite size: 40 nm) and controlling the sintering conditions, the dense HAp ceramic with relative density over 95% could be fabricated.32

As this example indicates, the sintering of nanometer-scaled HAp powder may occur at a comparatively lower temperature and, therefore, is advantageous to fabricate the dense HAp ceramic with inhibited grain growth.

Previously, Wakai and coworkers11,12 reported that the elongation of HAp ceramic fabricated by the hot isostatic pressing attained 153%, whereas that of HAp ceramic fabricated by pressureless sintering was as low as 35%. Apart from this report, few investigations on the deformation of HAp ceramic during heating have been carried out until now.13 On the basis of such background, this paper describes the fabrication conditions of dense HAp ceramic and evaluation of superplasticity in HAp ceramic fabricated by the pressureless sintering.

2. Experimental procedure

2.1 Fabrication of dense HAp ceramics

A commercially-available HAp powder was used in this research (HAp–100; Taihei-Kagaku Sangyo, Osaka). The impurities are chlorides (below 20 ppm), sulfates (below 50 ppm), metals such as lead (below 5 ppm), iron (below 10 ppm), arsenic (below 1 ppm), and magnesium (below 50 ppm). About 1.5 g of HAp powder was pressed uniaxially at 25 MPa to form a compact with a diameter of 15 mm and a thickness of 3 mm and, subsequently, cold-isostatically pressed at 50 MPa; the compact was fired in air at a temperature between 1000 and 1200°C for 5 h. The sintered compact was used for the measurement of relative density and observation of microstructure. On the other hand, a tensile-test specimen was fabricated as follows: about 4 g of the powder was pressed at 30 MPa uniaxially and then at 100 MPa cold-isostatically to form a bar-like HAp specimen; after the specimen was fired at a temperature described above, the sintered specimen with sizes of 28 mm × 10 mm × 3 mm were cut in order to fabricate the specimen for the tensile test. The specimen possessed a gauge length of 9 mm and the gauge length portion was polished using a diamond paste.
2.2 Evaluations
Phase identification was conducted using an X-ray diffractometer (XRD; RINT 2000V/P, Rigaku, Tokyo, 40 kV and 40 mA) with monochromatic CuKα radiation and a Fourier-transform infrared spectrometer (FT-IR; FT-IR8600PC, Shimadzu Corp., Kyoto). A specific surface area was measured using a Brunauer–Emmett–Teller method (BET); nitrogen was used as an adsorption gas. A primary particle size of the powder was calculated, assuming the particle shape to be spherical or cubic. The morphology of this HAp powder was studied using a transmission electron microscope (TEM; Model JEOL JEM-2011). The expansion-shrinkage of compressed powder (compact) was examined using a thermal-mechanical analyzer (TMA; Model TAS-100, Rigaku Co., Tokyo) at a heating rate of 10°C·min⁻¹; about 0.1 g of the powder was pressed uniaxially at 50 MPa to form a compact with a diameter of 5 mm and a thickness of 3 mm. The relative density of the sintered compact was calculated on the basis of bulk density and theoretical density (≈3.16 g·cm⁻³). The bulk density was measured by Archimedes method, using deionized water as a replacement liquid. The microstructure of the sintered compact was observed using a scanning electron microscope (SEM; Model S-4500, Hitachi, Tokyo, accelerating voltage, 15.0 kV), after the compact had been polished and then thermally etched below 100°C of the sintering temperature for 1 h. On the basis of the SEM micrographs, the average grain size was determined as π/2 times of the linear intercept length.

A tensile test at a constant cross-head speed (strain rate: 1.44×10⁻⁴ s⁻¹) was conducted in air at a temperature between 940 and 1100°C, using a universal testing machine (INSTRON-5851) equipped with furnace. A true stress-tensile strain curve was calculated on the basis of load-elongation curve, assuming that a uniform deformation occurs during the elongation. Here, the true stress was calculated on the basis of an initial cross section and strain.

3. Results and discussion

3.1 Properties of starting materials
The XRD pattern showed that the commercially-available powder was composed of only HAp. Moreover, the FT-IR pattern included the absorption peaks at 570, 600, 960, 1050 and 3570 cm⁻¹, and a broad absorption band in the range of 3000 to 4000 cm⁻¹.

Absorption peaks at 570 and 600 cm⁻¹ are assigned to the bending vibration of P–O and P=O groups; the peaks at 960 and 1050 cm⁻¹ are assigned to the stretching vibration of P–O and P=O groups, whereas the peak at 3570 cm⁻¹ is assigned to that of O–H group.¹⁵⁻¹⁷ The broad band in the range of 3000 to 4000 cm⁻¹ is assigned to the stretching vibration of H–O–H group.¹⁵⁻¹⁷ These results reveal that the chemical composition of the present HAp powder is stoichiometric and that no carbonate ions are included in the powder.

The specific surface area of this HAp powder was 69.4 m²·g⁻¹; the average primary particle size was 27.4 nm. SEM and TEM micrographs of the HAp powder are shown in Fig. 1. The SEM observation, primary particles got together to form agglomerates with sizes of several hundreds nanometers (Fig. 1(a)). The TEM observation showed that the rectangular-shaped primary particles with sizes of approximately 30 nm × 50 nm were present in the agglomerates (Fig. 1(b)). The diffraction pattern did not show distinct spots but show concentric rings (not shown in the present paper).

The primary particle size, calculated on the basis of the specific surface area and powder density, is almost in accordance with the particle sizes observed by the TEM. Results on electron diffraction indicate that these primary particles are polycrystalline and that these crystallites are randomly oriented.

3.2 Densification of HAp compact during the firing
Prior to checking the relative densities of HAp ceramics, the thermal expansion-shrinkage behavior of the HAp compact was examined using TMA. The results are shown in Fig. 2. The shrinkage of the HAp compact started at around 700°C and increased with temperature; most of the densification was completed at around 1000°C. On the basis of the rapid shrink-
around 900°C were observed. Fig. 4 shows the effect of firing temperature on the relative density of HAp compact. Note that the HAp compact was fired at each temperature for 5 h and that each relative density was plotted as an average of five values.

The above results indicate that most of the densification effect of pores present on grain boundaries. A rapid grain growth above 1100°C results in the entrapment of pores within grains, thereby accelerating the grain growth. On the basis of the above results, therefore, we conclude that the optimum firing temperature and time for the fabrication of dense and fine-grained ceramics are 1100°C and 5 h, respectively.

3.3 Tensile elongation of HAp specimen during heating
Since we determined the optimum firing conditions for the fabrication of dense HAp ceramic with small grains, we fabricated the specimen for the measurement of tensile strength and examined the superplasticity. The photograph of as-fabricated and deformed HAp specimens is shown in Fig. 5. The gauge length of the HAp specimen increased to 157.2 mm, the width was 6.6 mm, and the thickness was 3.2 mm. The thickness of the specimen was approximately 0.5 mm, which was closely packed with fine grains.

The elongations at 1050 and 1100°C exceeded 150%. The stress increased linearly until the tensile strain increased to 80%. The maximum true stress appeared at a tensile strain of 120 or 130%, and then the stress decreased gradually with further elongation. A typical SEM observation of the deformed HAp specimen is shown in Figs. 4. The cavities are found on grain boundaries after the elongation. A rapid grain growth above 1100°C results in the entrapment of pores within grains, thereby accelerating the grain growth.

The apparent changes in translucency seem to be attributed to the formation of cavities and grain growth during the elongation. The true stress-tensile strain curves at several temperatures are shown in Fig. 7, together with a typical SEM micrograph. The elongations at 1050 and 1100°C exceeded 150%. The stress increased linearly until the tensile strain increased to 80%. The maximum true stress appeared at a tensile strain of 120 or 130%, and then the stress decreased gradually with further elongation. A typical SEM observation of the deformed HAp specimen showed that a lot of damages due to the formation of cavities existed at the test temperature of 1100°C.

The cavities are found on grain boundaries after the elongation of the HAp specimen. This fact may also be confirmed by the observation that the parts of translucency were lost at the elongation, the shrinkage rate became maximum (0.91%·min⁻¹) at around 900°C, and then no appreciable changes in shrinkage rate occurred at temperatures exceeding 1000°C.

The above results indicate that most of the densification was completed when the HAp compact was heated up to 1000°C. This phenomenon is interpreted as the changes in sintering from initial/intermediate stages to the final stage at around 1000°C. This fact anticipates that the final stage of sintering may take place, when the heating temperature increases to 1000°C or higher.

On the basis of the above information, we investigated the effect of firing temperature on the relative density of compact and then determined the optimum sintering conditions for the fabrication of dense HAp ceramics. Results are shown in Fig. 3. Note that average relative density of the green compact was approximately 49.5%. The relative density of the sintered HAp compact increased with increasing firing temperature and attained 99.2%; on further firing up to 1200°C, however, little changes in relative density of the sintered HAp compact were observed.

SEM micrographs of the polished specimens are shown in Fig. 4. SEM micrograph of the HAp compact fired at 1050°C and 1100°C for 5 h showed that the polyhedral grains with sizes of approximately 0.5 μm were closely packed (Figs. 4(a) and (b)). SEM micrographs of the HAp compacts fired at 1150 and 1200°C for 5 h showed that the polyhedral grains with sizes of 1 to 3 μm were closely packed (Figs. 4(c) and (d)).

The effect of firing temperature on the average grain size of HAp compact is shown in Fig. 5. The grain size increased with increasing firing temperature; the slope of the linear relationship became steep when the firing temperature exceeded 1100°C. The grain growth inhibition observed in the temperature range of 1000 to 1100°C may be explained in terms of the "pinning" effect of pores present on grain boundaries. A rapid grain growth above 1100°C results in the entrapment of pores within grains, thereby accelerating the grain growth.
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Fig. 6. Photograph of the as-fabricated and deformed HAp specimens. (a) As-fabricated specimen, (b) Specimen deformed at 1000°C (Elongation: 118%), (c) Specimen deformed at 1050°C (Elongation: 156%), (d) Specimen deformed at 1100°C (Elongation: 157%).

Fig. 7. Effect of temperature on the true stress-tensile strain of the HAp specimens at the strain rate of 1.44 × 10^-4 s^-1, together with typical SEM micrograph. (a) 940°C, (b) 1000°C, (c) 1050°C, (d) 1100°C.

gauge length portion of the elongated HAp specimen. On the other hand, the elongation of specimen with the average grain size of 1.07 μm fabricated by pressureless sintering was previously reported to be 35%. The present elongation is 156% at 1050°C, which is approximately 4.5 times larger than that reported by them. Such larger elongation may be achieved not only by comparatively smaller number of defects present in the specimen but also by the smaller grain sizes.

SEM micrographs of the gauge length portion of deformed HAp specimen examined at 1000 and 1050°C are shown in Fig. 8, together with the grain size distribution. A significant grain deformation took place in the HAp specimen (Fig. 8 (a)); the cavity was observed in the elongated specimen (11). The average d_∥ (the grain size parallel to the tensile direction) and d_⊥ (the grain size perpendicular to the tensile direction) at 1000°C were 0.98 and 0.65 μm, respectively, whereas those at 1050°C were 1.73 and 1.39 μm, respectively; the ratios of d_∥ to d_⊥ at 1000 and 1050°C were 1.51 and 1.25, respectively.

Assuming that a cubic-shaped grain is deformed, the apparent intragranular strain, ε_e, is given by:

$$\epsilon_e = \frac{2}{3} \ln \frac{d_{\parallel}}{d_{\perp}}$$

(1)

From Eq. (1), the values of ε_e at 1000 and 1050°C are 0.274 and 0.146, respectively. On the other hand, the total strain, ε_T, is expressed as follows:

$$\epsilon_T = \ln \left( \frac{L_0 + \ell}{L_0} \right)$$

(2)

where L_0 is an original gauge length and ℓ is an elongation at the test temperature. On the basis of Eqs. (1) and (2), the contribution of grain boundary sliding to the total strain, A, may be defined as follows:

$$A = 100 \left( 1 - \frac{\epsilon_e}{\epsilon_T} \right)$$

(3)

The values of A at 1000 and 1050°C are 64.8 and 84.9%, respectively. These values indicate that the grain boundary sliding may be predominant during the deformation.

4. Conclusion

We investigated the optimum conditions for fabrication of the high-density and fine-grained HAp ceramic and examined the superplasticity. The results obtained in this study were summarized as follows:

(1) The compact was fired at a temperature between 1000 and 1200°C in order to fabricate the high-density and fine-grained HAp ceramics. The maximum relative density (99.2%) was achieved when the HAp compact was fired at 1100°C for 5 h. On the other hand, the grain growth was inhibited in the temperature range of 1000 to 1100°C; the average grain size was as small as 0.56 μm at the firing temperature of 1100°C. On further increase in firing temperature, however, the grain growth was promoted.
(2) The tensile elongation of this HAp specimen was examined at a temperature between 940 and 1100°C. Tensile elongations of these HAp specimens showed that the elongations tested at 1050°C and 1100°C attained 156 and 157%, respectively; the specimen tested at 1050°C contained a limited number of cavities on grain boundaries, whereas the specimen tested at 1100°C was observed to have a large number of cavities.

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References