DENSIFICATION AND SUPERPLASTICITY OF HYDROXYAPATITE CERAMICS - EFFECT OF FIRING CONDITIONS -

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Abstract Effect of firing conditions, *i.e.*, pressureless sintering, controlled-atmosphere sintering (water (H₂O) vapor) and hot-isostatic pressing, on the fabrication of high-density and fine-grained hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂: HAp) ceramic was examined; the tensile elongation of HAp ceramic during the heating was measured in order to evaluate the superplasticity. Relative densities of three types of HAp ceramics exceeded 99%; grain sizes were varied, according to the firing conditions: controlled-atmosphere sintering (1.09 μm) > hot-isostatic pressing (0.59 μm) > pressureless sintering (0.56 μm). Reflecting the magnitudes of grain sizes, the tensile elongations at 1100°C were arranged as follows: hot-isostatic sintering (176%) > pressureless sintering (156%) > controlled-atmosphere sintering (102%). The highest elongation of HAp ceramic fabricated by hot isostatic pressing was attributed not only to the small grain size but also to the elimination of defects.

INTRODUCTION

A superplastic deformation is expected as a novel technique to fabricate the desired and complex shapes of ceramics, because it is generally difficult to process the ceramic blocks through the cutting and grinding operations. In order to achieve the superplastic deformation 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 s⁻¹).¹⁾

A hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂: HAp) ceramic, which is biocompatible with bone,²⁾ is used for orthopaedic and dental implants, as a restorative material for the skull.³⁾ The excellent superplasticity of HAp ceramic may, therefore, be realized when the HAp ceramic is composed of submicrometer-scaled grain sizes. Previously, Wakai and coworkers^{2),4)} 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%. The present authors also examined the tensile elongations of HAp ceramic fabricated by pressureless sintering and found the maximum elongation as high as 157%. Such high elongation may be achieved not only by the high density but also by the small grain size (0.56 μm).⁵⁾ On the basis of such background, this paper describes the fabrication conditions of dense HAp ceramic and evaluation of superplasticity in HAp ceramic.

EXPERIMENTAL

1. Starting materials and fabrication of dense HAp ceramics

A commercially available HAp powder was used in this research (HAp-100; Taihei-Kagaku Sangyou, Osaka, Japan). The specific surface area of this HAp powder was $69.4 \text{ m}^2\cdot\text{g}^{-1}$; the average primary particle size was 27.4 nm. 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 by three techniques: (i) pressureless sintering, *i.e.*, the firing of compact at a temperature between 1000 and 1200°C for 5 h in air, (ii) controlled-atmosphere sintering *i.e.*, the firing of compact at a temperature between 1000 and 1200°C for 5 h in water (H₂O) vapor atmosphere, and (iii) hot-isostatic pressing *i.e.*, hot isostatic pressing of the pressureless-sintered HAp compact at 1000°C for 1 h under the pressure of 200 MPa in argon (Ar) atmosphere. Each sintered compact was used for the measurements of relative density and observation of microstructure.

A tensile-test specimen was fabricated as follows: the powder with the mass of 4 g was pressed at 50 MPa uniaxially and then cold-isostatically pressed at 100 MPa to form a bar-like HAp specimen. After the firing of specimen, the sintered bar-like specimen with a size of 28 mm × 10 mm × 3 mm was cut in order to fabricate a 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. Evaluations

Phase identification was conducted using an X-ray diffractometer (XRD; RINT 2100V/P, Rigaku, Tokyo, Japan, 40 kV and 40 mA) with monochromatic CuK α radiation. A specific surface area was measured using the Brunauer-Emmett-Teller method (BET). The morphology of this HAp powder was studied using a transmission electron microscope (TEM; Model JEOL JEM-2011). The relative density of the sintered compact was calculated on the basis of bulk density and theoretical density ($\approx 3.16 \text{ g}\cdot\text{cm}^{-3}$). The bulk density was measured by Archimedes method, using de-ionized 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). On the basis of the SEM micrographs, the average grain size was obtained as the $\pi/2$ time of the linear intercept length. A tensile-test at a constant cross-head speed was conducted in air at a temperature between 1000 and 1200°C, using a universal testing machine (INSTRON-5581). A true stress-tensile strain curve was calculated on the basis of load-elongation curve, assuming that a uniform deformation occurs during the elongation; the true stress was calculated on the basis of the initial cross section and strain.

RESULTS AND DISCUSSION

1. Densification and microstructure changes of HAp compact during the firing

We reported that most of the densification would be completed when the HAp

compact was heated up to 1000°C.⁵⁾ This phenomenon is caused by the change in the sintering mechanism from the initial/intermediate stages to the final stage at around 1000°C.⁶⁾ On the basis of this information, we investigated the effect of firing temperature on the relative density of compact through the techniques of pressureless sintering and controlled-atmosphere sintering, and then determined the optimum sintering conditions for the fabrication of dense HAp ceramics. Changes in relative density of sintered HAp compact during the firing in the water-vapor atmosphere are shown in Fig. 1, together with those in relative density of pressureless-sintered HAp compact.⁵⁾ Relative density of the HAp compact fired in the water-vapor atmosphere attained 99% at the firing temperature of 1000°C. Although it increased a little with increasing temperature, no distinct changes in relative density occurred for this HAp compact when the temperature exceeded 1050°C. This densification behavior was almost the same as that of the pressureless-sintered HAp compacts.

Changes in grain size of HAp compact during the firing in the water-vapor atmosphere are shown in Fig. 2, together with those in grain size of pressureless-sintered HAp compact. The rapid grain growth occurred in the water-vapor atmosphere when the firing temperature exceeded 1100°C, compared to the case of pressureless-sintered HAp compact.

Although no appreciable changes in relative density are observed in the temperature range of 1000 to 1100°C, a rapid grain growth occurs in the water-vapor atmosphere when the temperature exceeds 1100°C. This fact may be interpreted as the entrapment of pores within the grains, thereby accelerating the grain growth.⁵⁾

Typical grain-size distributions after the controlled-atmosphere sintering and pressureless sintering of HAp compacts are shown in Fig.3. No appreciable changes in grain-size distribution were found between two types of sintered HAp compacts. On further increase in sintering temperature up to 1150°C, however, the grain-size distribution of HAp compact after the controlled-atmosphere sintering became wider, compared to the case of pressureless-sintered HAp compact. This fact suggests that the

Fig. 1 Effect of firing temperature on the relative density of the HAp compact.
 ●: Pressureless sintering⁵⁾
 ○: Controlled-atmosphere sintering

Fig. 2 Effect of firing temperature on the average grain size of the HAp compact.
 ●: Pressureless sintering⁵⁾
 ○: Controlled-atmosphere sintering

mass transfer of component ions in HAp may be promoted during the firing of compact in the presence of water vapor. However, the difficulty in making a good contact of water vapor with HAp grains, especially inside of compact, causes the inhomogeneous sintering, resulting in the widening of grain-size distribution.

On the basis of the information about the relative density and grain-size distribution, we fabricated the specimens for the measurement of tensile strain, and examined the superplasticity.

As we reported before, the gauge length of pressureless-sintered HAp specimen increased to 157% with increasing test temperature up to 1100°C.⁵⁾ The true stress-tensile strain curves of controlled-atmosphere sintered HAp specimen at 1100°C are shown in Fig. 4, as a parameter of strain rate. The true strain of HAp specimen at the strain rate of $1.44 \times 10^{-4} \text{ s}^{-1}$ increased linearly until the tensile elongation increased to 75%. The elongation of HAp specimen increased to 102% at the strain rate of $2.88 \times 10^{-4} \text{ s}^{-1}$, whereas that of HAp specimen was reduced down to 80% at the rate of $4.32 \times 10^{-4} \text{ s}^{-1}$.

As shown above, the true strain of HAp specimen increased from 75% to 102% with increasing strain rate from $1.44 \times 10^{-4} \text{ s}^{-1}$ to $2.88 \times 10^{-4} \text{ s}^{-1}$. On further increase in the strain rate to $4.32 \times 10^{-4} \text{ s}^{-1}$, however, the true strain decreases to 80%. These elongations are lower than those of pressureless-sintered HAp specimens, which may be caused by the larger average grain size in the case of controlled-atmosphere sintering. Since we considered that the limited elongations of these HAp specimens were attributed to the larger grain size and wider grain size distribution, we examined again the tensile elongations by using the HAp specimen fired at 1050°C for 5 h in the water-vapor atmosphere. These specimens were dense and were composed of smaller grains (0.31 μm), compared to the case of HAp specimens fabricated by the atmosphere-control sintering at 1100°C for 5 h (grain size: 1.09 μm). True stress-tensile strain curves of these HAp specimens were also examined, as a parameter of strain rate at 1050°C. The true strain of HAp specimen at the strain rate of $1.44 \times 10^{-4} \text{ s}^{-1}$ increased linearly until the tensile elongation increased to 67%. The elongation at the strain rate of $2.88 \times 10^{-4} \text{ s}^{-1}$ was 90%, whereas that at the strain rate of $4.32 \times 10^{-4} \text{ s}^{-1}$ was 73%. The maximum elongation was achieved at the strain rate of $2.88 \times 10^{-4} \text{ s}^{-1}$ but was only 90%.

As shown above, elongations of HAp specimens fabricated by controlled-atmosphere sintering are limited, compared to the case of pressureless

Fig. 3 Grain-size distributions after the controlled-atmosphere sintering and pressureless-sintering of HAp compacts.

Fig. 4 Stress-strain curves of controlled-atmosphere sintered HAp specimens at the strain rate of (a) $1.44 \times 10^{-4} \text{ s}^{-1}$, (b) $2.88 \times 10^{-4} \text{ s}^{-1}$ and (c) $4.32 \times 10^{-4} \text{ s}^{-1}$. Note that the specimens were fabricated by the controlled-atmosphere sintering at 1100°C for 5 h.

Fig. 5 Stress-strain curve of the hot-isostatically pressed HAp specimen at 1100°C . Note that the strain rate was $1.44 \times 10^{-4} \text{ s}^{-1}$.

sintering. We furthermore examined the densification of HAp compact, using hot-isostatic press technique. The relative density of the hot-isostatically pressed HAp compact was 99.2%, whereas the grain sizes were distributed over the range of 0 - $1.60 \mu\text{m}$ with the average grain size of $0.59 \mu\text{m}$. True stress-tensile strain curves of the hot-isostatically pressed HAp specimens at the strain rate of $1.44 \times 10^{-4} \text{ s}^{-1}$ are shown in Fig. 5. The true strain of HAp specimen increased until the tensile elongation increased to 176%.

Wakai and coworkers^{2),4)} reported that the elongation of specimen with the average grain size of $1.07 \mu\text{m}$ fabricated by pressureless sintering was 35%. The present elongation is 176% at 1100°C , which is approximately 5 times larger than that reported by them. Such larger elongation may be achieved not only by the smaller grain sizes but also by comparatively smaller number of defects in the specimen.

The photograph after the deformation of HAp specimen was shown in Fig. 6,

Fig. 6 Photographs of (a) as-fabricated HAp specimen and (b) HAp specimen after the deformation at 1100°C . Note that the strain rate was $1.44 \times 10^{-4} \text{ s}^{-1}$.

Fig. 7 SEM micrograph of the hot-isostatically pressed HAp specimen after the deformation at 1100°C . Note that the strain rate was $1.44 \times 10^{-4} \text{ s}^{-1}$.

together with the as-fabricated specimen. Reflecting the high elongation (176%), the hot-isostatically pressed HAp specimen was significantly elongated.

A SEM micrograph of the gauge length portion of the deformed HAp specimen is shown in Fig. 7. The cavities were present after the deformation. Nevertheless, the amount of cavity was clearly smaller, compared to the case of pressureless-sintered HAp specimen.⁵⁾ This microstructure suggests that a further elongation may be achieved with decreasing the amount of cavity.

CONCLUSION

We investigated the superplasticities of high-density and fine grained HAp ceramics fabricated using several firing conditions. The results obtained in this study were summarized as follows:

- (i) Relative densities of HAp compacts after the controlled-atmosphere sintering and pressureless sintering at 1100°C for 5 h were almost the same (99.3% and 99.2%, respectively), whereas the average grain size of controlled-atmosphere sintered HAp compact (1.09 μm) was larger than that of pressureless-sintered HAp compact (0.56 μm). On the other hand, the relative density of HAp compact, which was fabricated by hot-isostatically pressing the pressureless-sintered compact at 1000°C for 1 h, was 99.2%, whereas the average grain size was 0.59 μm .
- (ii) Reflecting the magnitudes of grain sizes, the tensile elongations were arranged as follows: hot-isostatic sintering (176%) > pressureless sintering (156%) > controlled-atmosphere sintering (102%). The highest elongation of HAp ceramic fabricated by hot isostatic pressing seems to be attributed not only to the small grain size but also to the elimination of lattice defects.

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