Influence of $\beta$-tricalcium phosphate dispersion on mechanical properties of hydroxyapatite ceramics

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Mechanical properties of hydroxyapatite (HAp) ceramics and HAp/$\beta$-tricalcium phosphate ($\beta$-TCP) composites were measured at room temperature and at 1100°C to investigate influence of the $\beta$-TCP dispersion. HAp powder was synthesized by precipitation method, and the ceramics and its composites were obtained by sintering the powder. The HAp/30%$\beta$-TCP exhibited the best contribution to mechanical properties in this study. The compression test at 1100°C showed that the $\beta$-TCP dispersion reduced yield stress and work hardening of the HAp ceramics. Moreover, it was found that the composites were largely deformed without the change in grain shape and grain size. The result suggests superior superplasticity in the HAp/$\beta$-TCP composites to the HAp ceramics.

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1. Introduction

Calcium phosphate ceramics attract great interest as bone or tooth implant materials because of their excellent biocompatibility. Especially, hydroxyapatite (HAp) has been studied as a leading candidate since HAp ceramics were developed in 1970s. However, a clinical application of the ceramics is limited because their bending strength and fracture toughness are not high enough for an artificial bone or joint. For such the practical application, the mechanical properties must be improved. In addition, machinability of the ceramics should be also needed. Up to now, complex shapes in artificial human bones, joints and teeth have been obtained by grinding of bioceramics. However, near-net-shape processing by superplastic deformation is necessary for manufacturing of a wide variety of products in small quantities. Since superplastic deformation of ceramics can be made at high temperatures, it is important to understand high-temperature deformation behavior of the bioceramics.

Numerous studies have been reported on the mechanical properties of the HAp ceramics at room temperature. It has been revealed that the mechanical properties strongly depend on the conditions for synthesis and sintering of HAp powder, together with wide scattering in the strength and Young’s modulus. Some of the reports pointed out that dispersion of $\beta$-tricalcium phosphate ($\beta$-TCP) improved the mechanical properties. Raynaud et al. showed that HAp/10%$\beta$-TCP had the highest strength, whereas Akaô et al. reported that HAp/30%$\beta$-TCP exhibited the highest. There were differences in the synthesis and sintering conditions between two. Thus, influence of the $\beta$-TCP dispersion must also depend on these conditions. For fully understanding the influence, further studies are required in the HAp/$\beta$-TCP composites. Concerning high-temperature deformation behavior, Wakai et al. performed tensile tests at high temperatures in the HAp ceramics, and demonstrated their superplasticity. However, as far as the authors know, there have been no reports on the composites.

In this study, the HAp ceramics and HAp/$\beta$-TCP composites were fabricated under the different conditions from Raynaud’s and Akaô’s. The mechanical properties were measured at room temperature to study the influence of the $\beta$-TCP dispersion. Moreover, high-temperature compression tests were performed to reveal the high-temperature deformation behavior and to discuss superplasticity in the composites.

2. Experimental procedure

2.1 Fabrication of HAp ceramics and HAp/$\beta$-TCP composites

HAp powder was synthesized by precipitation method based on the reaction:

$$6(\text{NH}_4)\text{HPO}_4 + 10\text{Ca(OH)}_2 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 12\text{NH}_3 + 18\text{H}_2\text{O} \quad (1)$$

The procedure for preparing the powder was: (1) suspension of $0.258$ mol or $0.264$ mol Ca(OH)$_2$ (Wako Pure Chemical Industries, Ltd.) in $50$ ml distilled water and $150$ ml ethanol was vigorously stirred at room temperature, (2) solution of $0.15$ mol (NH$_4$)$_2$HPO$_4$ (Wako Pure Chemical Industries, Ltd.) in $500$ ml distilled water was slowly dropped to the calcium suspension under N$_2$ flow, (3) the reaction mixture was aged at room temperature for $48$ h and more, (4) the resultant precipitation was filtrated and washed a few times with distilled water, and (5) the filter cake was dried at $105^\circ$C and finally milled with a mortar and pestle.

When the HAp powder is non-stoichiometry, the HAp is partly decomposed into $\beta$-TCP during sintering, and consequently the HAp/$\beta$-TCP composite can be obtained. In this study, the HAp ceramics was made from the powder synthesized with an initial...
Ca/P molar ratio of 1.72, and its composites from the powders synthesized with an initial Ca/P molar ratio of 1.76. Figure 1 shows X-ray diffraction (XRD) patterns of the ceramics and composites measured using a diffractometer (Philips PW1840) with Cu Kα radiation. β-TCP content was estimated from a ratio of the highest peaks of HAp (211) and β-TCP (0210) to be 0%, 30%, and 48%, respectively.\(^9\) Relative density was measured by Archimedes method to be 92.7% for the HAp, 98.4% for the HAp/30%β-TCP and 98.2% for the HAp/48%β-TCP. The surfaces were polished and etched by 0.05% phosphoric acid solution, and microstructure was observed by scanning electron microscopy (SEM) (JEOL JSM–5300 LV). Figures 2(a) to (c) show the SEM images for the HAp, the HAp/30%β-TCP and the HAp/48%β-TCP, respectively. From Fig. 2(a), an average grain size was estimated by intercept method to be 0.8 μm. In Figs. 2(b) and (c), pores were uniformly dispersed over the surfaces. Since the β-TCP was selectively etched by the phosphoric acid, the original β-TCP areas were turned into pores. An area fraction of the pore was estimated to be 22% for the HAp/30%β-TCP and 50% for the HAp/48%β-TCP, which almost agrees with the β-TCP content from the XRD analysis. The SEM observation showed that the composites were fine-grained and dense, and that the β-TCP was uniformly dispersed in the composites.

2.2 Evaluation of mechanical properties

Rectangular specimens were prepared with 2.1 × 2.9 mm\(^2\) in cross section and 25–36 mm in length for material testing at room temperature. Bending strength and Young’s modulus were measured by 3-point bending test at a crosshead speed of 0.5 mm/min. The strength was calculated from the equation \(\sigma = 3PL/2wh^3\) where \(P\), \(L\), \(w\) and \(h\) are the fracture load, the span of 16 mm, the width and thickness of the specimen, respectively. For measurement of hardness and fracture toughness, Vickers hardness test was made with 9.8 N loads for 10 seconds. The fracture toughness was calculated from the following equation,\(^10\)

\[
K_{IC} = \frac{0.0667a^2H^0.6E^{0.4}}{c^{3.0}}
\]

where \(a\), \(c\), \(H\) and \(E\) are a half diagonal of the Vickers indent, the radius of the surface median crack, Vickers hardness and Young’s modulus, respectively.

A high-temperature compression test was carried out in air at 1100°C at a strain rate of 1.0 × 10\(^{-4}\) s\(^{-1}\). The rectangular specimen was prepared with 2 × 2 mm\(^2\) in cross section and 4 mm in length.

Fig. 1. XRD patterns of the HAp ceramics and the HAp/β-TCP composites obtained by sintering the synthesized powders at 1150°C (○: HAp, ●: β-TCP).

Fig. 2. SEM images of the etched surfaces for the HAp ceramics and the HAp/β-TCP composites.
Porosity and grain size. The dependence of bending strength on the decrease could be related to the increase of both the residual porosity and grain size as suggested by Raynaud et al., because neither the residual porosity nor grain size was increased in this study. Therefore, as described above, it was suggested that the decrease in strength was related to the increase in the number of microcrack.

**Figure 4** shows stress-strain curves in the compression test at 1100°C for the HAp ceramics and the HAp/β-TCP composites. The authors agree with the mechanism of increasing strength by Raynaud et al. However, the authors do not think that the mechanism of decreasing strength is related to the increase in residual porosity and grain size as suggested by Raynaud et al., because neither the residual porosity nor grain size was increased in this study. Therefore, as described above, it was suggested that the decrease in strength was related to the increase in the number of microcrack.

The HAp ceramics and HAp/β-TCP composites were fabricated by sintering the precipitated HAp powders. The 3-point bending strength, Young's modulus, Vickers hardness and fracture toughness were measured at room temperature to study the dependence on the β-TCP content. The mechanical properties were convexly increased with the β-TCP content. This is considered to be due to the two opposite reasons, the reinforcing effect and the microcrack. The compression test at 1100°C showed that the microcrack. The compression test at 1100°C showed that
the yield stress and work hardening were reduced by the $\beta$-TCP dispersion. Since the composites were largely deformed without growth and deformation of each grain, superior superplasticity will be exhibited in the composites.

References