

# Superplastic Deformation in Carbonate Apatite Ceramics under Constant Compressive Loading for Near-net-shape Production of Bioresorbable Bone Substitutes

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To produce carbonate apatite (CAP) ceramics with the desired complex shapes using superplastic deformation, deformation behavior of CAP ceramics under constant loading as well as physical properties after deformation were evaluated. Sintered CAP ceramics were plastically deformed in an electric furnace attached to a universal hydraulic testing machine under a constant load. CAP ceramics subjected to an initial compressive pressure of 10 MPa showed an appreciable amount of plastic deformation at temperatures ranging from 720 to 800°C. Plastic deformation increased with increasing temperature from about 10% to 70% after two hours of loading. X-ray diffraction analysis and SEM observation further revealed that some CAP crystals were elongated and aligned with the c-axis normal to the loading direction during superplastic deformation. It was thus concluded that a marked plastic deformation of about 70% at 800°C would be sufficient for near-net-shape production of bioresorbable CAP bone substitutes with complex shapes.

Keywords: Carbonate apatite, Superplasticity, Near-net-shape production

## INTRODUCTION

Carbonate apatite (CAP) is resorbed by osteoclasts<sup>1,2)</sup> and is similar in biocompatibility to hydroxyapatite (HAP)<sup>3)</sup> and  $\beta$ -tricalcium phosphate ( $\beta$ -TCP)<sup>4)</sup>. Although the bioresorption mechanism of CAP may be different from that of  $\beta$ -TCP<sup>5)</sup>, CAP dissolves to the same extent as  $\beta$ -TCP in weak acid media<sup>1)</sup>. These promising characteristics of CAP suggest the possibility of its wide use as a bioresorbable bone substitute<sup>6,7)</sup>. When CAP is used as a bone replacement material, near-net-shape production is required to fit the CAP ceramic material to a bone defect where shapes differ depending on each patient. However, the near-net-shape production of CAP ceramics without degrading their physical properties is difficult due to their brittle character and low fracture toughness<sup>8)</sup>.

It has been previously reported that sintered HAP ceramics<sup>9,10)</sup> showed marked plastic deformation, the so-called superplastic deformation, at around 1050°C under appropriate loading conditions similar to other ceramics<sup>11–14)</sup>. Recently, in a study<sup>15)</sup> aimed at developing CAP-bearing titanium implants, one of the present authors found that CAP particles also showed marked plastic deformation at 750°C. However, details of the conditions for marked plastic deformation sufficient for near-net-shape production of the CAP ceramics have not been clarified. With a view to producing CAP ceramics with the desired complex shapes using superplastic deformation, this study was undertaken to investigate the deformation behavior under constant loading, as well as the physical properties of CAP ceramics deformed.

## MATERIALS AND METHODS

### *Carbonate apatite specimens*

CAP was synthesized by mixing 8 L of 2 mol/L calcium nitrate solution and 2 L of 1.2 mol/L disodium hydrogen phosphate solution containing 6 mol disodium carbonate, for three days at 100°C and at pH of  $9.0 \pm 0.1$ <sup>8)</sup>. The pH was maintained constant by automatic addition of dilute sodium hydroxide. The precipitate was centrifuged, the supernatant decanted, and the centrifugate was washed 10 times with deionized, double-distilled water and then dried. The precipitate thus obtained was sieved using a 390-mesh sieve. The sieved material was placed in a metal mold (12 mm long and 8 mm in diameter), remolded at 50 MPa, and further compacted by cold isostatic pressing at 200 MPa. Rod specimens (9 mm long and 7 mm in diameter) were made with a lathe and then sintered at 700°C for two hours in air.

### *Plastic deformation*

Sintered CAP specimens were plastically deformed using a universal hydraulic testing machine (Servopulser EHF-FB5KN-10LA, Shimadzu Co., Kyoto, Japan) shown in Fig. 1. The alumina ceramic mold with the sintered CAP specimen was heated to temperatures ranging from 720 to 800°C in an electric furnace attached to the universal testing machine with a heating rate of 5°C/min. Within 30 seconds of reaching the prescribed temperature, a constant compressive load of 385 N, corresponding to an initial pressure of 10 MPa, was applied to the sintered CAP specimens through a 50- $\mu$ m-thick platinum foil. Changes in the length of the specimens were measured for two hours, while maintaining the

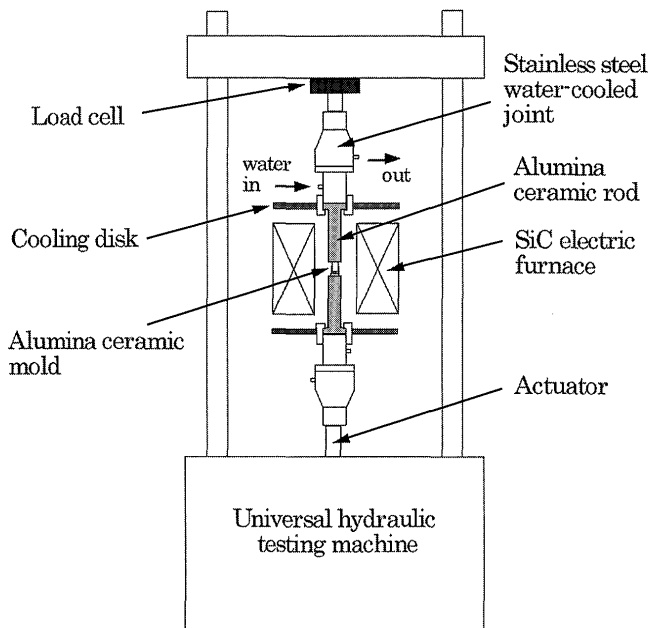


Fig. 1 Schematic illustration of a universal hydraulic testing machine with an SiC electric furnace used for superplastic deformation of carbonate apatite (CAP) ceramics.

constant load even after the start of deformation of the specimens. Control specimens were also heated with the same conditions without loading.

#### *Knoop hardness after plastic deformation*

The Knoop hardness number (KHN) of the deformed CAP specimens was determined on planes cut normal (normal plane) and parallel (parallel plane) to the loading direction. After plastic deformation, 1-mm-thick blocks were cut from the CAP specimens, and one surface of each block was polished with 0.1- $\mu\text{m}$  diamond paste. Ten indentations were made on the polished surface of each block using a microhardness tester (HMV-1, Shimadzu Co., Kyoto, Japan) with 2.94 N for 30 seconds, and the KHN was calculated from the length of a longer diagonal. Two blocks were used for each condition. KHN values of the control specimens were also measured.

#### *X-ray diffraction*

X-ray diffraction analysis was performed on the same blocks used for Knoop hardness measurements. A block — and even two or three blocks, if necessary — was mounted in an X-ray diffraction holder using utility wax. Diffraction patterns were recorded at a scanning rate of  $2^\circ/\text{min}$  with an X-ray diffractometer (XD-3A, Shimadzu Co., Kyoto, Japan) operated at 30 kV and 30 mA.

#### *Scanning electron microscopy (SEM) and average*

#### *grain size*

The polished surface of each CAP block was etched with a 0.05% phosphoric acid solution for 45 seconds. After washing and drying, the CAP specimens were ion sputter-coated with platinum (80%) and palladium (20%) and observed with a scanning electron microscope (S-4500, Hitachi Ltd., Tokyo, Japan). Twenty grains were selected from each SEM micrograph taken with  $\times 80,000$  magnification, and grain sizes in a direction parallel to the loading axis were evaluated by the linear intercept method<sup>16,17</sup>.

#### *Statistical analysis*

Both hardness and grain size data were assessed using a two-factor analysis of variance (ANOVA). For both sets of data, the two factors were plane type and temperature. If interaction between the plane type and temperature was significant, the data were rearranged for a one-factor design and one-way ANOVA was used instead. *Post hoc* testing was performed using Fisher's protected least significant difference (PLSD) test. A probability (*p*) value of less than 0.05 was considered significant.

## RESULTS

Figure 2 shows the time dependence of strain, which was defined as the amount of deformation induced by the applied load divided by the initial specimen length. Sintered CAP specimens subjected to an initial compressive pressure of 10 MPa showed an appreciable amount of plastic deformation at temperatures ranging from 720 to 800°C, and plastic deformation increased with increasing temperature from about 10% to 70% after two hours of loading. When loading was performed at 720°C, compressive plastic deformation tended to increase linearly, reaching about 10% after two hours of loading. At 800°C, the CAP specimen began to deform rapidly upon loading. Within 20 minutes, the deformation reached about 40% and continued to increase, reaching about 70% after two hours. When the amount of deformation at 800°C after two hours of loading was compared for different loads (data not shown), it was found that plastic deformation decreased with decreasing initial pressure — about 70%, 60%, and 40% at 10, 7.5, and 5 MPa respectively. Figure 3 shows the representative photographs of CAP specimens before plastic deformation (A), after 40% plastic deformation at 760°C (B), and after 70% plastic deformation at 800°C (C). In the 70% plastic deformed specimen, some cracks were observed.

Figure 4 shows the mean KHN values on the normal and parallel planes of the CAP specimens deformed at several temperatures. The mean KHN values of the control specimens were also included in the figure for comparison. As can be seen in Fig. 4,

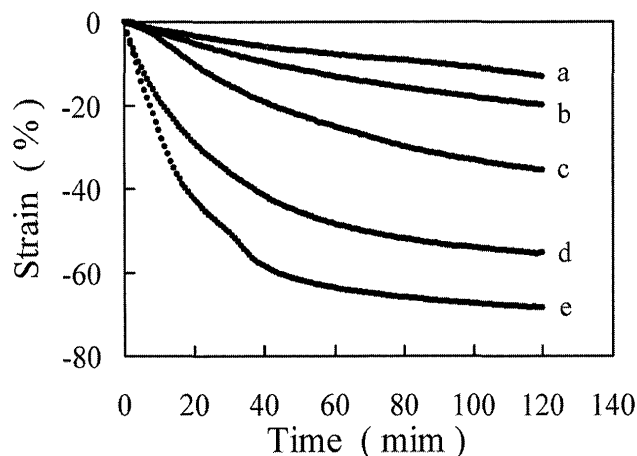


Fig. 2 Deformation behavior of the sintered CAP ceramics under a constant compressive load. The loading temperatures were 720 (a), 740 (b), 760 (c), 780 (d), and 800°C (e).

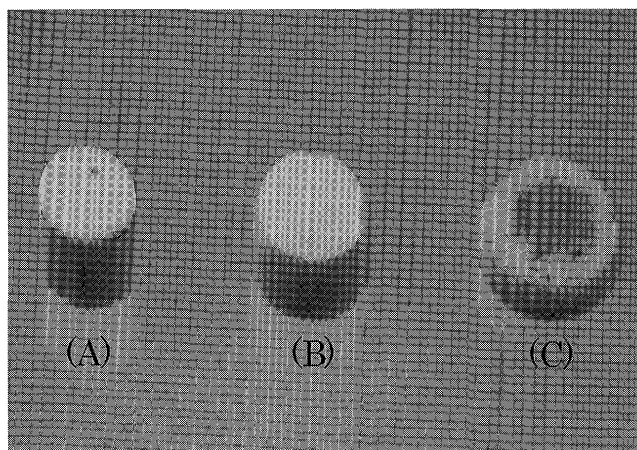


Fig. 3 Photographs of the CAP ceramics sintered at 700°C for 2 hrs (A), after superplastic deformation at 760°C for 2 hrs (B), and at 800°C for 2 hrs (C).

the mean values of KHN on the normal plane were significantly smaller than those on the parallel plane at all temperatures. Similarly, the mean KHN values on the normal plane were significantly smaller compared to those of the control at 740°C, 760°C, and 780°C. Furthermore, significant differences were found between the parallel plane and control at 720°C and 800°C.

Figure 5 compares the X-ray diffraction patterns on the parallel and normal planes of the CAP block specimens deformed at 800°C for two hours. The X-ray diffraction pattern of the control specimen was also included in the figure for comparison. The relative height of each reflection appeared to vary from plane to plane. For example, the height of (002) reflection at 25.6° ( $2\theta$ ) was greater on the parallel plane than on the normal plane, the latter in turn

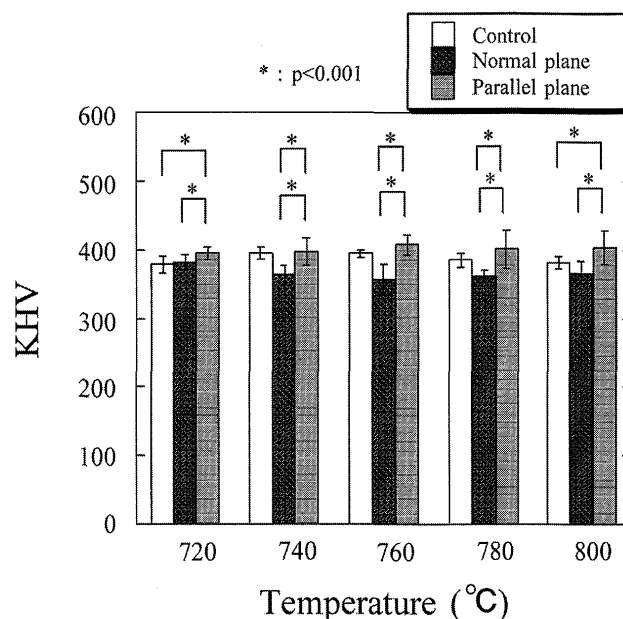


Fig. 4 Knoop hardness numbers measured on the normal and parallel planes of the CAP ceramics deformed at several temperatures for 2 hrs. Control specimens were heated with the same heating schedule for superplastic deformation without loading.

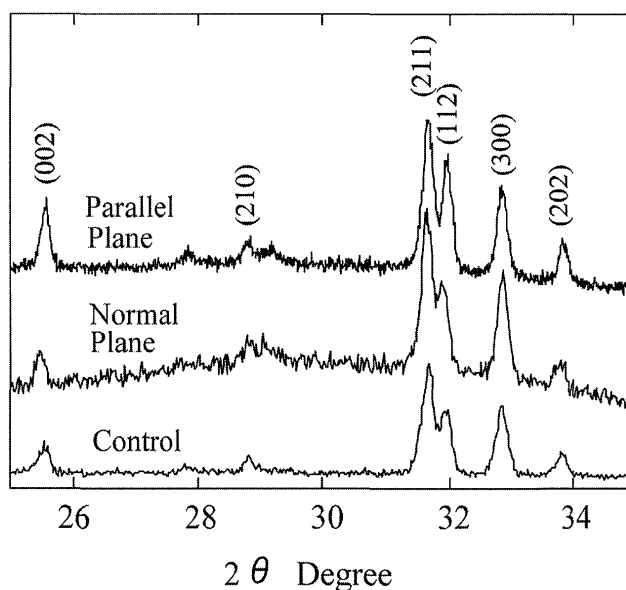


Fig. 5 X-ray diffraction patterns of the normal and parallel planes of CAP ceramics deformed at 800°C for 2 hrs.

being smaller than that on the control specimen. On the other hand, the height of (300) reflection at 32.9° ( $2\theta$ ) was greater on the normal plane than on the parallel plane and the control, indicating some CAP crystal orientation with the c-axis normal to the loading direction. The difference in relative intensity

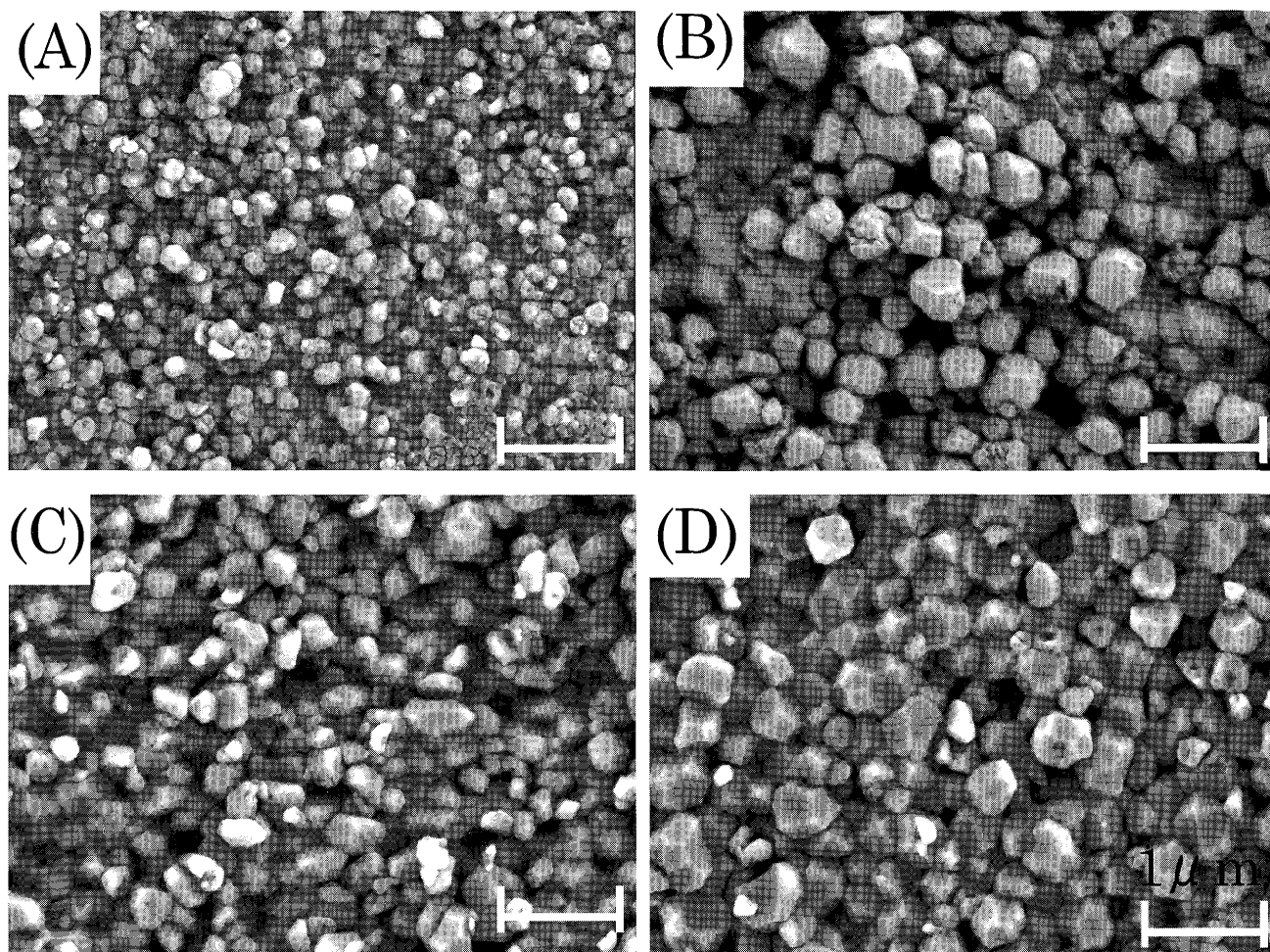


Fig. 6 SEM micrographs of CAP ceramic specimens sintered at 700°C for 2 hrs (A), the control (B), and the parallel (C) and normal (D) planes of the CAP ceramics deformed at 800°C for 2 hrs.

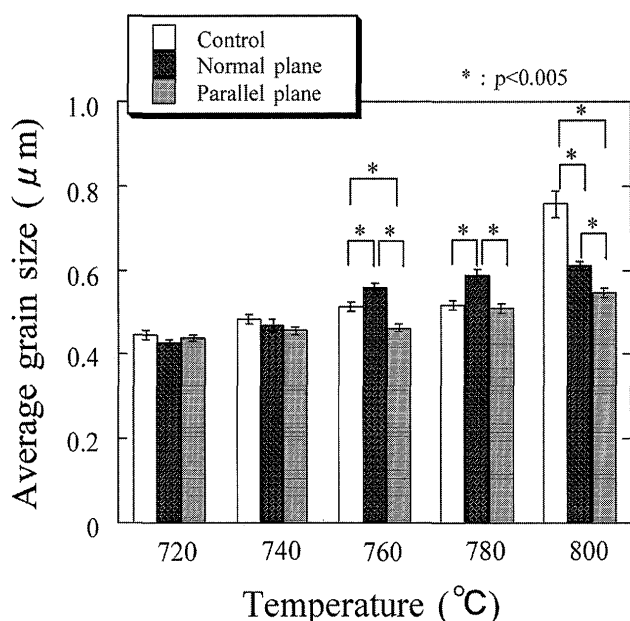


Fig. 7 Average grain sizes of the CAP ceramics deformed at several temperatures.

of (002) and (300) reflections between the parallel and normal planes, however, became less distinct as the temperature decreased such that the diffraction patterns were essentially the same at 720°C.

Figure 6 shows the SEM micrographs of the control (B) specimen, and parallel (C) and normal (D) planes of the CAP specimens deformed at 800°C for two hours. An SEM micrograph of a specimen sintered at 700°C for two hours (A) was also included in the figure for comparison. Figure 7 shows the average grain sizes evaluated on the control specimen and on the parallel and normal planes of the CAP specimens as a function of temperature. As can be seen in Fig. 6(A), prior to plastic deformation, the sintered CAP ceramic was composed of submicrometer-scale grains (average grain size: 0.39 μm), whereas in the CAP specimen heated at 800°C for two hours without loading (Fig. 6(B)), the average grain size increased significantly to 0.79 μm. On the other hand, when the sintered CAP ceramics were deformed at 800°C for two hours, the average grain

sizes on both the normal and parallel planes were significantly smaller than those of the control. It was found, therefore, that the marked plastic deformation observed at 800°C restrained the grain growth of the CAP ceramics. Moreover, the average grain size on the parallel plane (0.55  $\mu\text{m}$ ) was significantly smaller than that on the normal plane (0.61  $\mu\text{m}$ ). As shown by the white arrows in Fig. 6(C), some CAP crystals were elongated normal to the loading direction during superplastic deformation.

## DISCUSSION

Superplasticity is the phenomenon wherein polycrystalline solids subjected to an appropriate tensile stress at temperatures considerably lower than their melting points exhibit marked elongation without losing their physical properties<sup>11</sup>. Although there is no physical definition for determining superplasticity on the basis of elongation, metals are regarded as being superplastic when the elongation is approximately 300%, while brittle ceramics are regarded as being superplastic when the elongation exceeds 100%<sup>18</sup>. The occurrence of superplasticity and the mechanism of superplastic deformation have been reported for several ceramic materials, such as zirconia<sup>12</sup>, silicon nitride<sup>13</sup>, and HAP<sup>9,10</sup>. In these ceramics, it is thought that crystal grains undergo grain boundary sliding by closely adhering to each other, and that superplastic deformation is caused by rearrangement and growth of the grains<sup>16-20</sup>. Therefore, superplasticity is not a phenomenon peculiar only to a specific set of ceramics, but a more general phenomenon occurring in nearly all submicrogranular polycrystalline materials.

Previously, superplasticity was evaluated as the amount of elongation caused by tension. In the present study, the deformation of sintered CAP ceramics under constant compressive loading was evaluated instead. This was because one of our goals was to produce desired shapes with this material by compressive loading. Sintered CAP specimen subjected to an initial pressure of 10 MPa at 800°C showed marked plastic deformation of approximately 70%, which would be sufficient for near-net-shape production of bioresorbable CAP bone substitutes with complex shapes.

However, specimens showed rapid deformation immediately after load application at 800°C. Rapid deformation poses the risk of crack formation, as shown in Fig. 3(C), in which some cracks were evident in the specimen. The initial rapid deformation was followed by more gradual deformation, because the load-bearing area of the specimen increased as the deformation exceeded a certain level. As a result, the applied stress was reduced and the rate of deformation decreased after a substantial de-

mation (Fig. 2). If the applied load were increased in proportion to increases in the load-bearing area to maintain a constant stress, it was possible to plastically deform the specimens without generating flaws such as cracks.

In the case of silicon nitride ceramics, the mechanism of superplastic deformation has been reported to involve a residual amorphous grain boundary phase, which acted as a lubricant during grain boundary sliding upon heating. However, in oxide ceramics such as zirconia and HAP, no such amorphous phase was observed at the grain boundary<sup>22</sup>. In contrast to HAP, the CAP ceramics used in the present study could be sintered at temperatures approximately 400°C lower than that required for sintering HAP<sup>9</sup>. Since a large amount of sodium salt was used for synthesizing CAP, sodium rehenanite<sup>23</sup> produced might act as a sintering aid.

As can be seen in Fig. 4, sintered CAP specimens after superplastic deformation showed an increase in KHN on the parallel plane and a decrease in KHN on the normal plane at all temperatures. This suggested an increase in density and crystal growth in a specific direction. X-ray diffraction analysis revealed that the height of (002) reflection at 25.6° ( $2\theta$ ) was greater on the parallel plane than on the normal plane and for the control specimen, whereas the height of (300) reflection at 32.9° ( $2\theta$ ) was greater on the normal plane than on the parallel plane and for the control. Therefore, it was suggested that some CAP crystals were aligned with their c-axes normal to the loading direction. Moreover, SEM observation showed that the average grain size on the parallel plane was significantly smaller than that on the normal plane, indicating the elongation of CAP crystals normal to the loading direction during plastic deformation.

It could be concluded, therefore, that in the superplastic deformation of CAP ceramics, crystal grains exhibited grain boundary sliding with the amorphous phase acting as a lubricant. Superplastic deformation was then caused by the rearrangement and elongation of crystal grains normal to the loading direction.

## CONCLUSIONS

Sintered CAP ceramics subjected to an initial compressive pressure of 10 MPa showed an appreciable amount of plastic deformation at temperatures ranging from 720 to 800°C. During superplastic deformation, CAP crystals exhibited grain boundary sliding with the amorphous phase acting as a lubricant. Superplastic deformation was then caused by rearrangement and elongation of the crystal grains normal to the loading direction. Plastic deformation increased with increasing temperature from about

10% to 70% after two hours of loading. A marked plastic deformation of about 70% at 800°C would thus be sufficient for near-net-shape production of bioresorbable CAP bone substitutes with complex shapes.

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#### REFERENCES

- 1) Doi Y, Iwanaga H, Shibutani T, Moriwaki Y, Iwayama Y. Osteoclastic response to various calcium phosphates in cell cultures. *J Biomed Mater Res* 1999; 47: 424-433.
- 2) Kogaya Y, Hasegawa M, Uchida A, Doi Y. Ultrastructural characterization of tissue response to sintered carbonate apatite in rabbit bone. *Dent Mater J* 2006; 25: 482-492.
- 3) Gomi K, Lowenberg B, Shapiro G, Davies JE. Resorption of sintered synthetic hydroxyapatite by osteoclasts *in vitro*. *Biomaterials* 1993; 2: 91-96.
- 4) De Bruijn JD, Bovell YP, Davies JE, van Blitterswijk CA. Osteoclastic resorption of calcium phosphate is potentiated in postosteogenic culture conditions. *J Biomed Mater Res* 1994; 28: 105-112.
- 5) Nagayama M, Takeuchi H, Doi Y. Comparison of carbonate apatite and  $\beta$ -tricalcium phosphate (resorbable calcium phosphates) implanted subcutaneously into the backs of rats. *Dent Mater J* 2006; 25: 219-225.
- 6) Ellies LG, Nelson DGA, Featherstone JDB. Crystallographic structure and surface morphology of sintered carbonate apatites. *J Biomed Mater Res* 1988; 22: 541-553.
- 7) Barralet J, Akao M, Aoki H, Aoki H. Dissolution of dense carbonate apatite subcutaneously implanted in wistar rats. *J Biomed Mater Res* 2000; 49: 176-182.
- 8) Doi Y, Koda T, Wakamatsu T, Goto T, Kamemizu H, Moriwaki Y, Adachi M, Suwa Y. Influence of carbonate on sintering of apatites. *J Dent Res* 1993; 72: 1279-1284.
- 9) Wakai F, Kodama Y, Sakaguchi S, Nonami T. Superplasticity of hot isostatically pressed hydroxyapatite. *J Am Ceram Soc* 1990; 73: 457-460.
- 10) Tago K, Itatani K, Suzuki T, Sakka Y, Koda S. Densification and superplasticity of hydroxyapatite ceramics. *J Ceram Soc Japan* 2005; 113: 669-673.
- 11) Edington JW, Melton KN, Cutler CP. Superplasticity. *Prog Mater Sci* 1976; 21: 61-170.
- 12) Wakai F, Sakaguchi S, Matsuno Y. Superplasticity of yttria-stabilized tetragonal ZrO<sub>2</sub> polycrystals. *Adv Ceram Mater* 1986; 1: 259-263.
- 13) Panda PC, Raj R, Morgan PED. Superplastic deformation in fine-grained MgO·2Al<sub>2</sub>O<sub>3</sub> spinel. *J Am Ceram Soc* 1985; 68: 522-529.
- 14) Wakai F, Kodama Y, Sakaguchi S, Murayama N, Izaki K, Niihara K. A superplastic crystal composite. *Nature* 1990; 344: 421-423.
- 15) Teraoka K, Nonami T, Taoda H, Naganuma K, Yokogawa Y, Doi Y, Kameyama T. Carbonate apatite-bearing pure titanium implant. *Mat Res Soc Symp Proc* 2000; 599: 165-168.
- 16) Mendelson MI. Average grain size in polycrystalline ceramics. *J Am Ceram Soc* 1969; 52: 443-446.
- 17) Wurst JC, Nelson JA. Linear intercept technique for measuring grain size in two-phase polycrystalline ceramics. *J Am Ceram Soc* 1972; 55: 109.
- 18) The Ceramic Society of Japan. *Handbook of Ceramics*, 2nd ed, Gihoudou Shuppan, Tokyo, 2002, pp.345-348.
- 19) Kondo N, Ohji T, Wakai F. Strengthening and toughening of silicon nitride by superplastic deformation. *J Am Ceram Soc* 1998; 81: 713-716.
- 20) Ashby MF, Verrall RA. Diffusion-accommodated flow and superplasticity. *Acta Metall* 1973; 21: 149-163.
- 21) Gifkins RC. Grain-boundary sliding and its accommodation during creep and superplasticity. *Mater Trans* 1976; 7A: 1225-1262.
- 22) Wang JG, Raj R. Mechanism of superplastic flow in a fine-grained ceramic containing some liquid phase. *J Am Ceram Soc* 1984; 67: 399-409.
- 23) Doi Y, Shimizu Y, Moriwaki Y, Aga M, Iwanaga H, Shibutani T, Yamamoto K, Iwayama Y. Development of a new calcium phosphate cement that contains sodium calcium phosphate. *Biomaterials* 2001; 22: 847-854.