Fabrication of Hydroxyapatite Sintered Bodies with *c* Axis Orientation

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Hydroxyapatite (HAp) sintered bodies with *c* axis orientation were fabricated using *c* axis oriented plate-like HAp aggregates synthesized as described by us. The results of scanning electron microscopy and X-ray diffractometry indicated that the plate-like HAp aggregates accumulated horizontally to the flat surfaces of the cylindrical HAp sintered bodies and the *c* axis orientation of the HAp crystals perpendicular to the wide surfaces of the aggregates were maintained even after sintering.

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) is a main inorganic component of hard tissues in vertebrates and is used for artificial bones,[1] liquid chromatographic packing,[2] and scaffolds for tissue engineering.[3] HAp crystal has two surfaces with different electrical charges, i.e., positively charged *a*-surface adsorbing negatively charged molecules and negatively charged *c*-surface adsorbing positively charged molecules.[2] Therefore, regulating their morphology and agglomerate is very important to control their functions in medical and industrial use. Although many fabrication methods of HAp sintered bodies have been reported,[4–8] only a few reports on the control of crystal orientation in sintering are available.[9,10] In the present study, the HAp sintered bodies with *c* axis orientation were fabricated using *c* axis oriented HAp aggregates.

Plate-like HAp aggregates were synthesized by the hydrolysis of $CaHPO_4 \cdot 2H_2O$ at 25 and 100 °C for 1 h in 5 mass% NaOH solution as described in previous reports.[11,12] The aggregates hydrolyzed at 100 °C were composed of needle-like crystals aligned perpendicular to the wide surfaces of the plate-like aggregates.

HAp sintered bodies were fabricated using these aggregates. The HAp aggregates were decanted to eliminate fine particles and calcined at 750 °C for 3 h. The average particle sizes of the aggregates hydrated at 25 and 100 °C were estimated to be 60 and 48 µm, respectively. The calcined aggregates were suspended in acetone and the suspensions were poured into metal molds of 12 mm in diameter. After natural sedimentation of the suspensions, the excess acetone was excluded from the molds by gradual pressing of the suspensions by a pushrod. The green bodies obtained were sintered at 1100 °C for 3 h; the heating rate was 3 °C/min. The HAp sintered bodies fabricated from the aggregates hydrated at 25 and 100 °C are abbreviated as HAp_{25} and HAp_{100}, respectively. Their surfaces and the cross sections perpendicular to the flat surfaces, i.e., parallel to the pressing direction of the cylindrical HAp sintered bodies were observed by scanning electron microscopy (SEM, JEOL JMS-5600) and analyzed by X-ray diffractometry (XRD, Philips PW1700) to identify the crystal phases and to estimate the orientations. In the XRD measurements, the samples were held with clay on the holder. The orientation index of the plane $N_{h_ik_il_i}$, which is defined as Eq. 1, was calculated from the XRD pattern of either the surface or the cross section.

$$N_{h_ik_il_i} = \frac{R_{h_ik_il_i}}{R^0_{h_ik_il_i}} \qquad (1)$$

where $R_{h_ik_il_i}$ is an intensity ratio of the N plane and defined by Equation 2 and $R^0_{h_ik_il_i}$ is that of a random orientation obtained from JCPDS 9-432. The formula used is

$$R_{h_ik_il_i} = \frac{I_{h_ik_il_i}}{I_{h_1k_2l_3} + I_{h_2k_2l_2} + I_{h_3k_3l_3} + \cdots + I_{h_nk_nl_n}} \qquad (2)$$

where $I_{h_ik_il_i}$ is an intensity of the $h_ik_il_i$ diffraction.

Figure 1 shows the XRD patterns of the surfaces and cross sections of the HAp_{25} and HAp_{100}. The HAp_{100} was identified as a HAp single phase by XRD; however, the HAp_{25} was composed of HAp and a small amount of β-$Ca_3(PO_4)_2$ produced by the decomposition of the HAp aggregates. Figure 2 indicates the relations between orientation and diffraction indexes of HAp_{25} and HAp_{100}. Regarding HAp_{100}, the 002 and 004 diffractions on the surface, corresponding to the *c*-plane, were much higher than those on the cross section whereas the 200 and 300 diffractions on the surface, corresponding to the *a*-plane, were much lower. On the contrary, the differences of the diffraction indexes between the surface and cross section of the HAp_{25} demon-

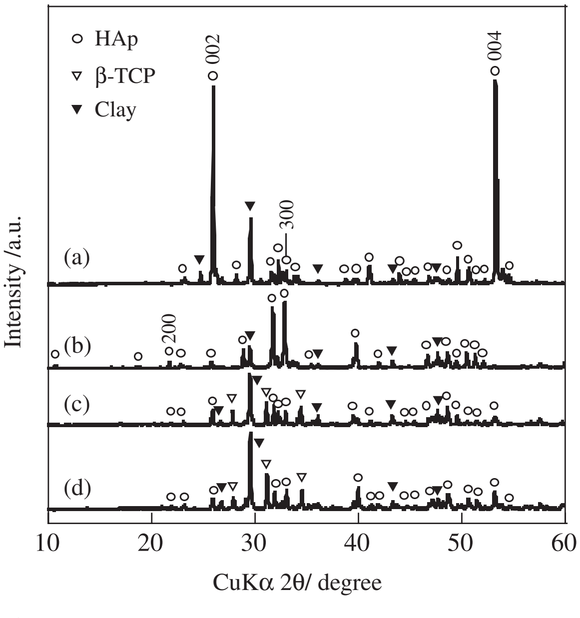

Figure 1. XRD patterns of (a) surface and (b) cross section of HAp_{100} and (c) surface and (d) cross section of HAp_{25}. The clay peaks were ascribed to clay for sample fixation.

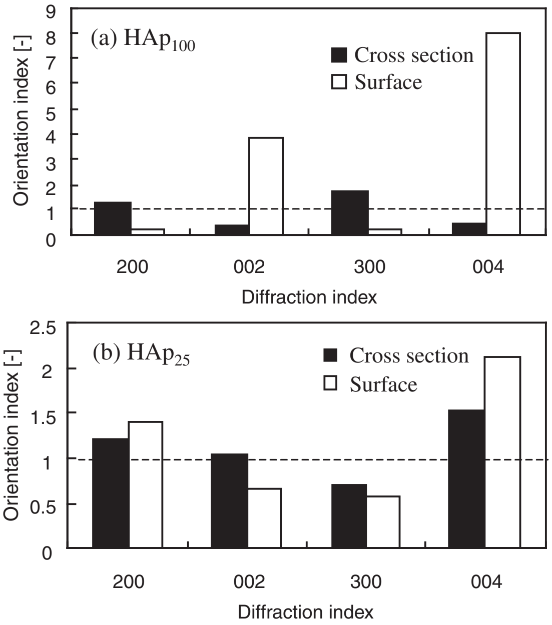

Figure 2. Relationships between orientation and diffraction indexes of (a) HAp_{100} and (b) HAp_{25}.

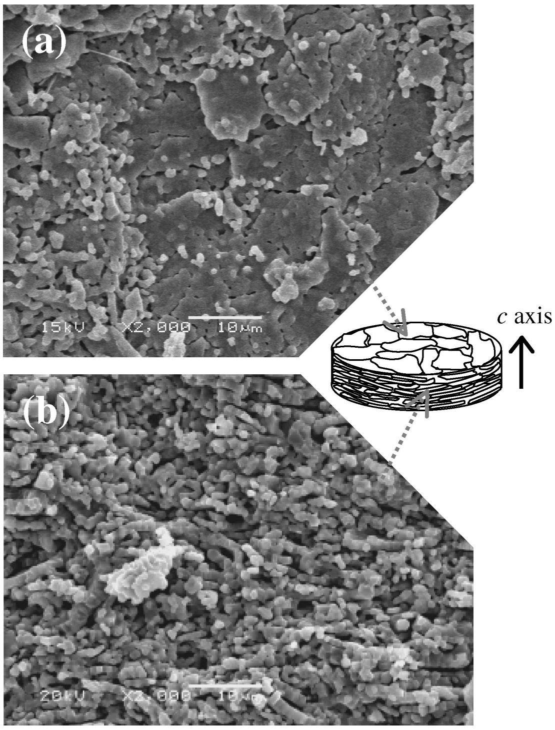

Figure 3. SEM photographs of (a) surface and (b) cross section of HAp_{100}.

strated no tendency, i.e., the HAp sintered body had no obvious crystal orientation. SEM photographs of the surface and cross section of HAp_{100} are shown in Figure 3. The plate-like HAp aggregates, whose morphology was shown in our previous papers,[9,10] were accumulated horizontally to the flat surface of the cylindrical HAp sintered body. These results indicate that the *c* axis orientation of HAp aggregates is maintained even after sintering.

The SEM observation also demonstrated that the aggregates in the sintered body had a few connections each other. The relative density of the HAp sintered bodies was estimated to be 81%. This low relative density in comparison to ordinary HAp sintered bodies was attributed to the restriction of sintering with crystal growth in the space among the plate-like HAp aggregates as similar as usually observed in sintering of fibrous HAp crystals.[13]

In summary, HAp sintered bodies were successfully fabricated using *c* axis oriented HAp aggregates. The *c* axis orientation of HAp aggregates was maintained even after sintering and the plate-like HAp aggregates were accumulated horizontally to the flat surface of the cylindrical HAp sintered body. The HAp sintered body with successful *c* axis orientation is expected to be useful to control biological reactions.

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References

1 L. L. Hench, *J. Am. Ceram. Soc.*, **81**, 1705 (1998).
2 T. Kawasaki, *J. Chromatogr.*, **544**, 147 (1991).
3 H. Ohgushi and A. I. Caplan, *J. Biomed. Mater. Res.*, **48**, 913 (1999).
4 M. Jarcho, C. H. Bolen, M. B. Thomas, J. Bobick, J. F. Kay, and R. H. Doremus, *J. Mater. Sci.*, **11**, 2027 (1976).
5 M. Akao, H. Aoki, and K. Kato, *J. Mater. Sci.*, **16**, 809 (1981).
6 G. De With, H. J. A. Vandijk, N. Hattu, and K. Prijs, *J. Mater. Sci.*, **16**, 1592 (1981).
7 K. C. B. Yeong, J. Wang, and S. C. Ng, *Mater. Lett.*, **38**, 208 (1999).
8 L. M. Rodriguez-Lorenzo, M. Vallet-Regi, and J. M. F. Ferreira, *Biomaterials*, **22**, 583 (2001).
9 M. Aizawa, H. Ueno, and K. Itatani, *Mater. Integr.*, **12**, 75 (1999).
10 K. Inoue, K. Sassa, Y. Yokogawa, Y. Sakka, M. Okido, and S. Asai, *Key Eng. Mater.*, **240-242**, 513 (2003).
11 K. Ohta, M. Kikuchi, J. Tanaka, and H. Eda, *Chem. Lett.*, **2002**, 894.
12 K. Ohta, M. Kikuchi, J. Tanaka, and H. Eda, *Key Eng. Mater.*, **240-242**, 517 (2003).
13 M. Aizawa, F. S. Howell, K. Itatani, Y. Yokogawa, K. Nishizawa, M. Toriyama, and T. Kameyama, *J. Ceram. Soc. Jpn.*, **108**, 249 (2000).