Orientation of Hydroxyapatite C-Axis under High Magnetic Field with Mold Rotation and Subsequent Sintering Process

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Orientation of hydroxyapatite (HAp) crystals is one of the promising ways to utilize their anisotropic nature of chemical and biological properties. On the other hand, the development of super conducting magnet technology enables to introduce a high magnetic field which can control crystal orientation of non-magnetic materials with magnetic anisotropy. In this study, a horizontal 10 T static magnetic field was imposed on slurry containing HAp crystals under the horizontal mold rotation during slip casting process so as to introduce *c*-axis orientation for some amount of crystals in the sample, and then it was sintered in atmosphere without the magnetic field. From SEM observation and X-ray diffraction, it has been found that the *c*-axis of pillar shape HAp crystals in the sample treated with the magnetic field and the mold rotation were oriented to a particular direction and it was enhanced by the subsequent sintering process, while the *c*-axis crystal orientation of the sample treated without the magnetic field and with the mold rotation was not observed before and after the sintering.

(Received May 10, 2005; Accepted September 5, 2005; Published November 15, 2005)

Keywords: hydroxyapatite, crystal orientation, high magnetic field, slip casting, mold rotation, sintering

1. Introduction

Hydroxyapatite (HAp), which is a raw material of artificial bones, scaffolds, adsorbents in liquid chromatography and so on, exhibits an anisotropic adsorbing nature depending on crystal planes, stemmed from its anisotropic crystal structure. For example, acidic proteins whose isoelectric points are lower than 7 are mainly adsorbed onto the *a,b*-plane of HAp while basic ones onto the *c*-plane.^{1,2)} In addition, hard tissues of vertebrates consisting of HAp and type-I collagen have a self-organized structure in which both the *c*-axis of HAp crystals and the longitudinal axis of collagen fibrils align parallel to the direction on which the maximum stress acts in a bone.³⁾ These facts tell that controlling crystal orientation imparts specific functionality to HAp, which is indispensable for the improvement of bioactivity and adsorption in biomaterials and adsorbents. On the other hand, it is possible to control crystal orientation of non-magnetic materials such as metals,^{4,5)} ceramics^{6,7)} and polymers⁸⁾ by imposition of a high magnetic field if these materials have magnetic anisotropy. In the case of HAp, the *a,b*-plane orientates perpendicular to the direction of a magnetic field.^{9,10)} However, the orientation of *c*-plane is uncontrollable by imposing a static magnetic field because the *c*-axis of HAp can arbitrary rotate within the plane perpendicular to the magnetic field.

In this study, a mold containing HAp particles dispersed in water was rotated in a horizontal plane under the imposition of a horizontal static magnetic field during slip casting, and then the obtained HAp cake was sintered at atmospheric pressure without the magnetic field. The crystallographic orientation of HAp on the surface of the sample was evaluated by X-ray diffraction (XRD) and the appearance of HAp particles was observed by a scanning electron microscope (SEM) before and after the sintering.

2. Experimental

The experimental procedure is summarized in Fig. 1. HAp powders (Taihei Chemical Industrial Co., LTD HAP-200, Particle diameter: 5–20 μm), distilled water and a dispersant were mixed to prepare slurry with a solid loading of 30 mass%. After milling for 3 h, the slurry was poured into

Fig. 1 Experimental flow.

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a mold with an inside diameter of 22 mm and a capacity of $1.5 \times 10^3 \text{ mm}^3$ made of gypsum. The mold was put on a rotating platform set at the center of a bore in a superconducting magnet and a slip casting of the slurry was carried out with or without a 10 T static magnetic field in horizontal direction. The rotating velocity of the platform was set to 0.3 rad/s. The reason why the mold rotation is required for obtaining uni-directional crystal orientation was described in the previous paper.¹¹⁾ After the slip casting, the cake dried in air for 24 h (dia. 22 mm, thickness = 10 mm) was used for evaluating the degree of crystal orientation and observing particle shape by using XRD and SEM, respectively. Then the cake was sintered at 1423 K for 2 h at atmospheric pressure without the magnetic field and the sample rotation. Then the degree of crystal orientation and the observation of particle shapes in the sintered samples were again examined.

3. Results and Discussion

3.1 Magnitude of magnetization force

The profile of a magnetic flux density, $|B|$ and a product of the magnetic flux density and its gradient, $|B \cdot dB/dx|$, which were generated by a superconducting magnet (TOSHIBA Corporation, TM-12VH10), are shown in Fig. 2. The maximum magnetic flux density is 10 T at $x = 0 \text{ mm}$ (the

Fig. 2 Distribution of magnetic flux density, B , and product of the magnetic flux density and its gradient, BdB/dx .

center of the rotating platform) and the maximum value of $|B \cdot dB/dx|$ is $110 \text{ T}^2/\text{m}$ at $x = 30 \text{ mm}$ (the edge of the rotating platform). In a non-uniform magnetic field, it is considered that not only the magnetic torque but also the magnetization force may act on HAp particles. By adopting the values of magnetic susceptibility of HAp and water are -1.24×10^{-6} , and -9.0×10^{-6} , respectively, the maximum magnetization force acting on the HAp particle dispersed in a water can be evaluated as 720 N/m^3 at $x = 30 \text{ mm}$ and the gravity force is $2.0 \times 10^4 \text{ N/m}^3$. Thus, the effect of the magnetization force could be ignored in this experiment.

3.2 Experimental results

A SEM image of HAp powder after the milling is shown in Fig. 3(a). The shape of each particle is a hexagonal pillar with a breadth of about 100 nm and a length of about 200–300 nm. The powder diffraction pattern is given in Fig. 3(b), where the diffraction intensities of each peak well agree with those given in JCPDS card #9-432.

Figure 4 shows the SEM images on the surface of the samples before and after the sintering, where no magnetic field was imposed during the slip casting. Before the sintering, small HAp grains with randomly directed orientation are seen [Fig. 4(a)]. After the sintering, grain sizes grew and the pillar shape was deformed to a spherical one [Fig. 4(b)]. The grain orientation is not seen in the samples produced without the imposition of the magnetic field. The XRD pattern was measured on the samples obtained before and after the sintering. Figure 5(a) shows the XRD pattern of the sample without the magnetic field. The difference between the XRD profiles in the raw powder given in Fig. 3(b) and that for the sample obtained after the slip casting, which is shown in Fig. 5(a), is not clear. However, the a,b -planes at the surface of the sample might slightly increase by the slip casting without the magnetic field. Figure 5(b) shows the XRD profile of the sintered sample treated without the magnetic field. Again, few differences are seen between the samples obtained before and after the sintering. This result tells us that the crystal orientation does not appear in the sample produced without the imposition of the magnetic field.

The SEM images on the upper surface of the sample before the sintering, obtained by imposing the magnetic field during

Fig. 3 HAp powder used in this experiment. (a) SEM image (b) XRD profile

Fig. 4 SEM images of the sample treated with $B = 0$ T. (a) before sintering (b) after sintering

Fig. 5 XRD profiles of the samples. (a) $B = 0$ T before sintering, (b) $B = 0$ T after sintering

Fig. 6 SEM images of the sample treated with $B = 10$ T. (a) before sintering (b) after sintering

Fig. 7 SEM images of the sample treated with $B = 10$ T. (a) before sintering (b) after sintering

the slip casting, mainly shows a circular shape of HAp particles as shown in Fig. 6(a) and that on its cross-sectional area indicates a pillar shape which aligns parallel to the gravitational direction as shown in Fig. 6(b). Then the crystal orientated its longitudinal axis parallel to the vertical axis. Figure 7 shows the SEM images of the sample obtained after the sintering. On the upper surface, the diameter of grains increase to about 1–2 μm and the hexagonal grain shape is clearly observed as shown in Fig. 7(a). On the other hand, plate-like or pillar-like grains are mainly seen on the cross section of the sintered sample as shown in Fig. 7(b). From these two SEM images, it is understood that hexagonal cylindrical grain growth whose hexagonal plane is parallel to the upper surface was intensified during the sintering. Figure 8 shows the XRD patterns on the surface of the sample before and after the sintering. The observed surface is in parallel to the direction of the imposed magnetic field. In Fig. 8(a), the diffraction intensities of c -plane such as (002), (004) increase compared with those for the sample treated without the magnetic field, while those of (200), (300), (310), which are perpendicular to the c -plane decrease. After the sintering, only the peaks corresponding to c -plane such as (002) and (004) appear and other peaks almost disappear as

shown in Fig. 8(b). Thus the initial c -axis orientation which had been introduced by the slip casting was enhanced during the sintering process. This can be explained from the viewpoint of the grain boundary energy.¹²⁾ Since the low-angle grain boundary energy is lower than that of large-angle grain boundary, the grain growth of oriented crystals was preferentially occurred in comparison with the non-oriented ones. From the XRD analysis and the SEM observation, it has been concluded that the hexagonal plane of the grains observed on the upper surface of the sintered sample is the c -plane of HAp. That is, the c -axis of HAp crystals corresponding to the longitudinal direction of grains aligns uni-axially parallel to the particular direction.

4. Conclusion

The high magnetic field and the mold rotation were imposed on HAp slurry during slip casting to control crystal orientation of HAp particles. We successfully introduced c -axis crystal orientation of pillar shape HAp particles in the cake while the sample treated without the magnetic field was not observed crystal orientation. Furthermore, hexagonal cylindrical grain growth was intensified and c -axis orientation was enhanced during sintering without the magnetic field imposition.

Acknowledgement

This research was partially supported by the Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Exploratory Research, (No. 16656209), "Creation of Nature-Guided Materials Processing" of the 21st Century COE Program and research support program of SEKISUI CHEMICAL Company.

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Fig. 8 XRD profiles of the samples. (a) $B = 10\text{ T}$ before sintering, (b) $B = 10\text{ T}$ after sintering