CONTROL OF PARTICLE ORIENTATION OF HYDROXYAPATITE UNDER A HIGH MAGNETIC FIELD

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Abstract A hydroxyapatite is the main component of a human's body and teeth, and a crystal orientation is required because it has different properties for each plane. In this study, a hexagonal rod-like powder was used. The aqueous suspension was prepared and was slipcast with and without a high magnetic field. The particle orientation was confirmed by the XRD patterns on the planes parallel and perpendicular to the direction of the magnetic field. It is confirmed that the particles orientate with the c-plane parallel to the magnetic field.

INTRODUCTION

A hydroxyapatite (HAP, Ca10(PO4)6(OH)2) is the main component in bones and teeth of vertebrates, and has an excellent biocompatibility1), and studies to apply HAP for artificial bone and tooth implant have been conducted2-5). HAP has a hexagonal crystal, and it is known that the a,b-plane is bio-active and c-plane is bio-inert6). Therefore, a crystal orientation is required to apply HAP for a biomaterial. Several studies of controlling the particle orientation of HAP have been conducted before6-10). Recently, a high magnetic field of 10 T is available without liquid helium due to the development of superconducting technology. The possibility of particle orientation in a magnetic field has now appeared. The principle of this method is applying the magnetic anisotropy of the crystal. The materials with non-cubic crystal structures have anisotropic magnetic susceptibilities, $\Delta \chi = \chi_{a,b} - \chi_{c}$, associated with their crystal structure, where $\chi_{a,b}$ and $\chi_{c}$ are the susceptibilities of the a,b-axis and c-axis, respectively. The energy of anisotropy is given as11,12):

$$\Delta E = \Delta \chi V B^2 / 2\mu_0$$

(1)

where $V$ is the volume of the materials, $B$ is the applied magnetic field, and $\mu_0$ is the permeability in a vacuum. When $\Delta E$ exceeds the thermal motion at room temperature, a magnetic torque occurs and the particles rotate to the angle minimizing the system.
energy. To align the particles in a high magnetic field, colloidal processing is available\textsuperscript{(11,13)}. The method of colloidal processing is as follows: dispersing particles in a liquid by pH control\textsuperscript{(14)} or addition of a polyelectrolyte\textsuperscript{(15)}, and compacting by slip casting. It was first reported that the textured alumina was obtained by colloidal processing in a high magnetic field, followed by heating\textsuperscript{(16)}. In this study, we examined the particle orientation of HAP in a high magnetic field using rod-like particles.

**EXPERIMENTAL**

A hexagonal rod-like powder, R-HAP (Taihei Chemical Industrial Co., HAP200), was used. The BET surface area (Coulter Co. SA3100) was measured, and the particle size was calculated.

The aqueous suspension with a 30 vol\% solid content was prepared. The ammonium polycarboxylate (Toagosei Co. A-6114) was used as the dispersing agent. An appropriate amount of the dispersing agent was determined by measuring the viscosity (Toki Industrial Co. R-500) of the suspension as a function of the amount of the dispersant. The appropriate amount was determined to be 1.2 wt\%. The \(\zeta\)-potential (Otsuka Electronics LSPZ-100) was determined for two samples; one is R-HAP with an appropriate amount of dispersing agent and the other is R-HAP without it. An ultrasonic horn was used for 10 min for re-dispersing the suspension. After stirring at room temperature for 12 h, the suspension was degassed in a vacuum. Slip casting was operated with and without an applied high magnetic field (10 T). The magnetic field was applied in directions of parallel and perpendicular to the slip casting. The CIP treatment was done on green compacts at 400 MPa for 10 min. The sintering was conducted at fixed temperatures between 1073-1573 K for 4 h in air without a magnetic field. The density of the sintered compacts was measured by Archimedes' method. An X-ray diffraction (XRD) analysis was carried out for the cross-sectional planes which were parallel and perpendicular to the slip casting. The 002 and 300 reflections were focused on, and the orientation index of each plane was calculated using the following equations\textsuperscript{(3)}:

\[
N_{hkl} = \frac{F_{hkl}}{F_{0hkl}} \quad (2)
\]

\[
F_{hkl} = \frac{I_{hkl}}{\sum I_{h,k,l}} \quad (3)
\]

where \(F_{0hkl}\) is obtained as standard data from ICDD 9-0432 and \(I_{hkl}\) is the intensity of the reflection of the \(hkl\) plane. When the orientation index is 1.0, particles are not oriented. When the index is greater or smaller than 1.0, it suggests that the particles...
are oriented to the degree of the calculated index.

RESULTS AND DISCUSSION

Fig. 1 is an SEM image of the R-HAP powder. The BET surface area was 3.2 m$^2$/g and the calculated particle size was 0.58 µm. From the SEM image, it is seen that the R-HAP powder is partially agglomerated. Fig. 2 shows the ζ-potential of the suspension as a function of pH. It is seen that the negative absolute value of the ζ-potential increases by the addition of a dispersing agent. This result illustrated that the carboxyl groups of the ammonium polycarboxylate adsorb on the surface of the particles. The improvement in stability of the suspension is due to the high dispersion of particles by adsorption of the carboxyl groups on the particles, and the stereophonic obstacle of the adsorbed carboxyl groups also contributes to the stability of the suspension. Fig. 3 shows the relative density of the sintered body as a function of the sintering temperature. Above the temperature of 1473 K, the relative density reached 97%.

Fig. 4 shows the XRD patterns and orientation index of the slipcast material without a magnetic field. The orientation indices of the 002 and 300 reflections are nearly 1.0 and show little difference between the T- and S-planes. This indicates that the particles are randomly oriented. Fig. 5 shows the XRD patterns and orientation index when the direction of the magnetic field was parallel to the casting direction. From Fig. 5(b), it is seen that the orientation index of the 002 reflection increases in the S-plane and that of the 300 reflection increases in the T-plane. This indicates that HAP particles orient with the c-plane parallel to a magnetic field. Fig. 6 shows the XRD patterns and orientation index when the direction of the magnetic field was
perpendicular to the casting direction. From Fig. 6(b), it is seen that the orientation index of the 002 reflection increases in the T- and S1-planes and that of the 300 reflection increases in the S2-plane. This also indicates that the HAP particles orient with the c-plane parallel to the magnetic field. On the basis of these results, it is possible to control the particle orientation by controlling the direction of the applied magnetic field.

Fig. 4 (a) X-ray diffraction patterns of R-HAP sintered at 1573K without a magnetic field and (b) Orientation index calculated.

Fig. 5 (a) X-ray diffraction patterns of R-HAP sintered at 1573K, where the magnetic field was parallel to the fluid and (b) Orientation index calculated.
To improve the orientation, the R-HAP powder was milled. The BET surface area of the milled powder, indicated as M-HAP, was 7.2 m$^2$/g and the calculated particle size was 0.28 μm. To compare the extent of the particle orientation between R-HAP to M-HAP sintered at 1573 K, the orientation indices of each powder were compared. Fig. 7 shows the orientation indices of M-HAP and R-HAP when the magnetic field is parallel to the casting direction. In the S-plane, the orientation index of the 002 reflection of R-HAP is 1.66 and that of M-HAP is 1.80. In the T-plane, the orientation index of the 300 reflection of R-HAP is 2.16 and that of M-HAP is 2.52. This indicates that the extent of particle orientation of M-HAP was higher than that of R-HAP. This result suggests that the dispersion of each particle in the suspension is improved by milling the partially agglomerated particles.

REFERENCES

1) Z. He, J. Ma, C. Wnag, Biomaterials, 26, p1613(2005)
Fig. 7 Comparison of orientation indices of M-HAP and R-HAP sintered at 1573K, where the magnetic field was parallel to the fluid.