Hydrothermal Solidification of Calcium Phosphate Treated by Dry Ball Milling

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Influence of processing time of dry ball milling for β-TCP (Ca₃(PO₄)₂) on strength development with hydrothermal treatment was investigated. β-TCP was ground by dry ball milling for 0.5–8 h and formed by uniaxial pressing. The formed body was hydrothermally treated at 180°C for 6 h under saturated steam pressure. In all cases, hydroxyl apatite (HAP: Ca₁₀(PO₄)₆(OH)₂) was formed by hydrothermal treatment. The flexural strength increased with milling time and reached the maximum value of 23.6 MPa for 2 h. The increase in the flexural strength by dry ball milling was caused by the increase of bulk density and contact point of fine HAP crystals.

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1. Introduction

Since the waste disposal is one of the serious problems, we are urged to grapple with the recirculation of waste sludge. The amount of sewage sludge disposed in year reaches 30 million tons.1) The incineration disposal is a main method in the intermediate processing for the sewage sludge in Japan. About 14 % of the ash is utilized as the construction materials, and about 70% of the ash disposed to landfill.2) As it becomes more difficult to secure the landfill site for waste disposal, we need to increase the ratio of effective waste utilization.

The incineration ash of sewage sludge contains much amount of phosphorus compounds as β-tricalcium phosphate (β-TCP: Ca₃(PO₄)₂) and CaO-Al₂O₃-SiO₂-P₂O₅ glass.3,4) Therefore, we have tried to solidify the ash of sewage sludge by the formation of hydroxyl apatite (HAP: Ca₁₀(PO₄)₆(OH)₂) through the hydrothermal treatment in order to utilize the ash as a building material. HAP is known as the biocompatible materials like inorganic constituents of bones and teeth, and is utilized as the implant materials.5,6) Absorption agent of heavy metal,7) chromatography for separation and purification of functional protein.8) Therefore, many researchers have investigated the control of the porosity9) and the increase of flexural strength10,11) of HAP body. The hydrothermal treatment has attracted the attention of researchers, because the energy consumption of the hydrothermal treatment is relatively small and the environment impact is kept very low.12) However, the flexural strength of test specimen solidified by the formation of HAP through hydrothermal treatment was not enough for strength of building materials.13) Therefore, it is significant for us to increase the strength of test specimen solidified by HAP formation through the hydrothermal treatment.

The control of crystal morphology precipitated by the hydrothermal treatment is significant for increasing of the strength development. Particularly, kinetics of dissolution of starting material is one of the most significant points in its morphology control. The kinetics of dissolution of starting material is affected by the specific surface area of materials, processing temperature, pH, dissolution time and so on.14) The dry ball milling treatment is one of the methods of the control of the particle size and specific surface area of material. Synthesized β-TCP which is one of the phases constituted incineration ashes of sewage sludge was used as a starting material.

In this paper, the influence of processing time of dry ball milling on the mean particle size and specific surface area of β-TCP powder and the flexural strength of the specimen after the hydrothermal treatment were investigated.

2. Experimental Procedures

2.1 Synthesis of β-tricalcium phosphate

Dibasic calcium phosphate dehydrate (CaHPO₄·H₂O; DCPD, reagent grade Wako Pure Chemical Industries, Ltd.) and calcium hydroxide (Ca(OH)₂, UBE Material) were used as the starting materials. DCPD and Ca(OH)₂ were weighed to obtain mixtures with Ca/P atomic ratio of 1.5 stoichiometric ratio of β-TCP. The mixture was heated at 1000°C for 3 h. Heating rate was 5.5°C/min.

2.2 Dry ball milling of β-tricalcium phosphate powder

β-TCP powder was weighed out 100 g and was put in the aluminum milling pot (4.3 L) with aluminum balls of 3.0 kg. The powder was ground by dry ball milling for periods ranging from 0.5 h to 8 h (t₀ = 0.5, 1, 2, 4, 8 h). The particle size distribution of β-TCP powder was measured by laser diffraction (MICROTAC RHA9230—X100, Nikkiso). The specific surface area of β-TCP powder was determined by B.E.T. using nitrogen gas (Macsorb HM model-1201, Mountech).

2.3 Forming and Hydrothermal Treatment

Distilled water was added to achieve 10 mass% of the β-TCP powder. After mixing, the 10 mm×15 mm×40 mm rectangular test specimens were formed by uniaxial pressing (30 MPa) and hydrothermally treated under saturated steam pressure at 180°C for 6 h. The hydrothermally treated bodies were dried at 80°C for 2 days. The phases of test specimens were identified by XRD analysis (Model RAD-B, Rigaku). The strength of the specimens were tested by a three-points flexural strength test (support distance, 30 mm; crosshead speed, 0.5 mm/min; number of specimens, 5; Model TENSION TSM500, A&D), and their bulk density was calculated from the mass and dimensions. The microstructures of the test specimens were observed by SEM (Model S-4700, Hitachi), and the pore size distribution were determined by mercury intrusion porosimetry (Model PoreMaster—33P, Quantachrome, U.S.A.). The experimental procedure of this study was shown in Fig. 1.

3. Results and discussion

3.1 Characterization of β-TCP powder processed by the dry ball milling

Figure 2 shows the XRD patterns of the β-TCP powder synthesized and processed by the dry ball milling. In the all specimen, β-TCP was the only observed phase in the specimens.
The size of β-TCP particles decreased with processing time of dry ball milling (Fig. 3). The mean particle size indicated 28.0 μm in the case of \( t_1 = 0 \) h, and drastically decreased to 2.8 μm by 0.5 h of the dry ball milling, and tended to decrease very slightly for longer milling times. This result suggested that the starting stage of the dry ball milling process (from \( t_1 = 0 \) h to 0.5 h) affected the decrease of the mean particle size. The specific surface area of β-TCP powder increased with the decrease of the mean particle size (Table 1). The SEM observation was carried out to clarify the mechanism of changing of the mean particle size with the processing time of dry ball milling (Fig. 4). In the case of \( t_1 = 0 \) h, β-TCP powder had a lot of pores inside of themselves (Fig. 4(a)), and had traces of crystal growth on the surface of β-TCP particles and grain boundary among each β-TCP particles (Fig. 4(b)). The 0.5 h milling resulted in the disappearance of pores. These results suggested that the drastic decrease of the mean particle size from \( t_1 = 0 \) h to \( t_1 = 0.5 \) h was caused by separation of each β-TCP particles on grain boundary. In the case of \( t_1 = 0.5 \) h and above, the mean particle size gradually decreased with processing time of dry ball milling, suggesting that milling process acted on the grinding of the β-TCP particles separated than the separation of the each β-TCP particles.

![Flow chart of experimental procedure](image1)

![XRD patterns](image2)

![SEM photographs](image3)

![Particle size distribution](image4)

**Fig. 1.** Flow chart of the experimental procedure.

**Fig. 2.** XRD patterns of (○) β-TCP processed by dry ball milling for 0–8 h.

**Fig. 3.** Variation of the particle size distribution of β-TCP powder with milling time. (The value in parentheses indicates the mean particle size.)

<table>
<thead>
<tr>
<th>Milling time / h</th>
<th>Mean particle size / μm</th>
<th>Specific surface area / m²·g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>28.0</td>
<td>1.06</td>
</tr>
<tr>
<td>0.5</td>
<td>2.8</td>
<td>2.51</td>
</tr>
<tr>
<td>2</td>
<td>2.2</td>
<td>2.84</td>
</tr>
</tbody>
</table>

**Table 1.** The mean particle size and specific surface area of β-TCP powder processed by ball milling for 0–2 h.
3.2 Characterization of the specimens after hydrothermal treatment

3.2.1 Phases formed through hydrothermal treatment

The phases of formed through hydrothermal treatment were identified by XRD (Fig. 5). In the all specimen through hydrothermal treatment, \( \beta \)-TCP and HAp were observed as two phases constituted the specimens. However, the peak intensity of HAp decreased with ball milling time.

3.2.2 The flexural strength and bulk density

The variations of flexural strength and bulk density of the specimens with processing time of dry ball milling was shown in Fig. 6. The bulk density of specimens with milling process for \( \beta \)-TCP powder was higher than that made without milling process. The bulk density drastically increased from 1.54 g/cm\(^3\) to 1.65 g/cm\(^3\) by the 0.5 h dry ball milling and scarcely increased for longer milling times. The reason of the increase of bulk density was caused by the disappearance of pores in \( \beta \)-TCP powder which led to decrease of packing density. The flexural strength of the specimens was also increased by the milling process of \( \beta \)-TCP powder. The strength drastically increased from 6.8 MPa to 23.6 MPa by the dry ball milling for 2 h and scarcely increased for longer milling times. This result suggests that the variation of strength change with ball milling corresponds to one of bulk density.

The pore size distribution was investigated in order to clarify the mechanism of increase of flexural strength and bulk density with milling times (Fig. 7). For all the specimens, the pore diameter peaks shifted toward finer diameters by hydrothermal treatment. The peak shift by hydrothermal treatment was caused by formation of HAp. After hydrothermal treatment, the pore diameter peaks shifted toward finer diameters with time of the milling process. The peak shift by time of the milling process was caused by the decrease of the mean particle size of \( \beta \)-TCP. The width of peak in the all cases with the milling process was narrower than one of no milling. This phenomenon was caused by the homogeneous distribution of the particle size of \( \beta \)-TCP by the milling. The homogeneous distribution of the particle size caused the homogeneous dissolution of \( \beta \)-TCP powder, and the HAp crystals formed by hydrothermal treatment had homogenous morphology.

The total pore volume of the specimens using the milling \( \beta \)-TCP after hydrothermal treatment was lower than in the case without the milling process. Since the pore was the one of fracture source, the decrease of total pore volume led the increase of flexural strength. The morphology of HAp crystals were observed with SEM (Fig. 8). The needle-like HAp crystals identified by XRD and its morphology were formed by hydrothermal treatment.

The needle-like HAp crystals were intertwined another one to form around the aggregate remained \( \beta \)-TCP. This result suggests that the strength of the specimen after hydrothermal treatment was increased by the intertwining of each needle-like crystals of HAp.

In the comparison of the length of HAp crystals in specimen, the length decreased with the milling time. In the case of no milling \((t_1 = 0 \text{ h})\), the length of HAp crystal was 1.81 \( \mu \text{m} \), with the increase of milling time, the crystal length decreased, 1.21 \( \mu \text{m} \) at 0 h, 1.11 \( \mu \text{m} \) at 2 h and 0.65 \( \mu \text{m} \) at 8 h. The decrease of the length with milling time was caused by the increase of specific surface area of \( \beta \)-TCP powder by the milling. The dissolution rate of \( \beta \)-TCP powder increase with the increase of specific surface area, resulting in the formation of nucleation of HAp rather than the crystal growth.

The above results indicate that the increase of flexural
strength with the dry ball milling was caused by the formation of fine needle-like crystals of HAp and the increase of bulk density of the specimens by the milling. The decrease of crystal size led the increase of contact points among HAp crystals. The increase of bulk density also affected the decrease of total pore volume which was fracture source.

4. Conclusions

Influence of processing time of dry ball milling for \( \beta \)-TCP on strength development with hydrothermal treatment was investigated. The mean particle size of \( \beta \)-TCP powder decreases with the milling time. On the other hand, the specific surface area increases with the milling time. The flexural strength of the hydrothermally treated specimen increases with the milling time with the formation of HAp and reached the maximum value of 23.6 MPa for 2 h. The increase of flexural strength with the dry ball milling was caused by the formation of fine needle-like crystals of HAp and the increase of bulk density of the specimen by the milling.

References