研 究

Control of the Microstructure of Porous Tricalcium Phosphate:
Effects of addition of Mg, Zn and FeMasanobu Kamitakahara^{☆1} Chikara Ohtsuki^{☆1}, Makoto Oishi^{☆1}, Shin-ichi Ogata^{☆1},
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SYNOPSIS

Tricalcium phosphate (TCP) ceramics are known as biodegradable materials for use as bone substitutes in orthopedic applications. We recently reported the fabrication of porous α -TCP ceramics with continuous pores ranging from 10 to 50 μm , through a conventional sintering process using a slurry consisting of β -TCP and potato starch. α -TCP shows higher solubility than β -TCP. Therefore, one can expect that biphasic porous ceramics consisting of α - and β -phases of TCP will allow controlled degradation in the body. In the present study, we attempted to synthesize a porous TCP body consisting of a mixture of α - and β -TCP with an additive of Mg, Zn or Fe. It was revealed that the porosity and phase of porous tricalcium phosphate can be controlled by the addition of these additives. The addition of Mg was most effective in decreasing the porosity and α -TCP content. When the Mg content was 0.1 mass%, a porous body consisting of α - and β -TCP with continuous pores ranging from 10 to 50 μm can be prepared by the conventional sintering method.

KEY WORDS

Tricalcium phosphate, porosity, biphasic

1 Introduction

Bone consists of hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and collagen¹⁾. It supports our body and enables us to perform various motions. When the bone is damaged by disease or an accident, our motion is restricted. Defects of bones have been repaired by autogenous or allogenic bones. In the case of autogenous bones, however, a healthy part of the patient is damaged and the amount of bone available is limited. In the case of allogenic bones, infections are sometimes caused through viruses, bacteria, etc. Therefore, artificial materials are needed to repair the bone defects. Some calcium phosphates such as hydroxyapatite²⁾ (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and tricalcium phosphate³⁾ (TCP, $\text{Ca}_3(\text{PO}_4)_2$) are used for bone repair. Although HAp shows osteoconductivity, its biodegradability is low. Therefore, HAp remains in the body for a long time after implantation.

Tricalcium phosphate (TCP) ceramics are known as biodegradable materials for use as bone substitutes in orthopedics^{4,5)}. The porous body of TCP is gradually dissolved away from the bony defect during bone repair, leading to its substitution by bone regeneration due to invasion of body fluid and cells related with formation and decomposition of bone tissue. It is therefore worth fabricating porous ceramics with biodegradable components.

We recently reported the fabrication of porous α -TCP ceramics with continuous pores ranging from 10 to 50 μm ^{6,7)}, through a conventional sintering process using a slurry consisting of β -TCP and potato starch. α -TCP shows higher solubility than β -TCP^{8,9)}. Therefore, one can expect that biphasic porous ceramics consisting of α - and β -phases of TCP will allow controlled degradation in the body. It was previously reported that additives such as Mg¹⁰⁾ and Zn¹¹⁾ raised the transformation temperature from β - to α -phase of TCP. However, the effect of additives on the fabrication process of the porous TCP bodies has not been clarified yet. In the present study, we attempted to synthesize a porous TCP body consisting of a mixture of α - and β -TCP by addition of Mg, Zn and Fe.

2 Experimental procedure

2.1 Sample preparation

Trimagnesium phosphate octahydrate ($\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$: Nacalai Tesque Inc., Japan), triiron phosphate octahydrate ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$: Kanto Chemical Co. Inc., Japan), or trizinc phosphate tetrahydrate ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$: Kanto Chemical Co. Inc., Japan) powders were mixed with β -TCP (Nacalai Tesque Inc., Japan) powder in a polyvinyl chloride bottle to obtain compositions with Mg, Zn, or Fe

concentrations ranging from 0.1 to 1.0 mass%. The mixed powder was stirred with ion-exchanged water for 1 day, and dried at 60 °C for 3 days. The obtained powder was mixed with potato starch (Nacalai Tesque Inc., Japan) at a mass ratio of 1 : 1 for 30 minutes by using a ceramic mortar and the ultrapure water was added to the mixed powder to form a slurry. The slurries were then impregnated into a polyurethane sponge 15 × 15 × 15 mm³ and dried at 60 °C for 1 hour. The samples were fired to 1000 °C at a rate of 5 °C/min and kept at that temperature for 3 hours to burn out the sponge and starch using a muffle furnace (KDF-S70, Denken Co. Ltd., Japan) in a draft chamber. After air-cooling in the furnace, the sample was moved to a SiC furnace (SC-2025D, Motoyama Co. Ltd., Japan) and sintered at 1400 °C for 12 hours, followed by cooling to room temperature in the furnace. Fig. 1 shows the sintering program of the samples. The resulting porous ceramic samples doped Mg, Zn and Fe were labeled as Mg(x), Zn(x) and Fe(x), respectively, where x means the concentration of each element as mass%. TCP(0) was also fabricated using the same procedure without any additive.

2.2 Characterization

The apparent porosity of the samples was calculated by measuring the weight and volume. The morphology of the samples was examined by scanning electron microscope (SEM, S-3500N, Hitachi Ltd., Japan). The

Fig.1 Sintering program.

crystalline phase of samples was identified by powder X-ray diffraction (XRD, MXP3V, Mac Science Co., Japan) with CuK α radiation. The phase contents of α - and β -TCP in samples were semi-quantitatively determined by comparing the heights of their maximum peak (α -TCP: $2\theta = 30.75^\circ$, β -TCP: $2\theta = 31.00^\circ$).

3 Results and Discussion

Fig. 2 shows SEM photographs of the samples TCP(0), Mg(0.1) and Mg(1.0). The pores 10 – 50 μ m in diameter were observed for TCP(0) and Mg(0.1), while they were not observed for Mg(1.0). The pores decreased with the addition of Mg. The same tendency was also observed for Zn and Fe. Fig. 3 shows the porosity of the samples. The sample without an additive, denoted as TCP(0), had 79% porosity, while the porosities of Mg(0.1), Fe(0.1) and Zn(0.1) were approximately 80%, irrespective of their kinds, similar to that of TCP(0). However, when the amount of additive became more than 0.1 mass%, the porosity significantly decreased. When the Mg content was 1.0 mass%, the porosity was less than 20%. The addition of Mg was most effective in decreasing the porosity.

Fig.3 Porosities of the samples as a function of additive content.

Fig.2 SEM photographs of the samples with different Mg contents.

Figs. 4–6 show the powder X-ray patterns of samples containing Mg, Fe, and Zn, respectively. All of the samples were composed of only α - and/or β -TCP. In TCP(0), only α -TCP was detected. Not only α -TCP but also β -TCP was detected in Mg(0.1) and Mg(0.5), while only β -TCP was identified in the Mg(1.0). The β -TCP content increased with increasing Mg content. When Zn content was 0.1 mass%, only α -TCP was detected. Both α -TCP and β -TCP were detected in Zn(0.5) and Zn(1.0). The content of β -TCP increased with increasing Zn content,

Fig. 4 Powder X-ray diffraction patterns of the samples with different Mg contents.

Fig. 5 Powder X-ray diffraction patterns of the samples with different Zn contents.

and that of α -TCP was as little as 10% when Zn content was 1.0 mass%. Both α - and β -TCP were detected in Fe(0.1), Fe(0.5) and Fe(1.0). The content of β -TCP increased with increasing Fe content, and Fe(1.0) contained only small amount of α -TCP. Fig. 7 summarizes the phase contents of α - and β -TCP in samples. The content of β -TCP in the samples increased by increasing the amount of additives. The addition of Mg was most effective in increasing the content of β -TCP.

It was previously reported that the additives, such as Mg¹⁰⁾ and Zn¹¹⁾, raised the transformation temperature from β - to α -phase of TCP. The increase in the transformation temperature provides the samples with a high content of β -TCP phase. This should also affect the porosity of the samples. It is considered that the phase transformation

Fig. 6 Powder X-ray diffraction patterns of the samples with different Fe contents.

Fig. 7 Phases of the samples as a function of additive content.

from β - to α -TCP prevents further densification¹²⁾. Based on this theory, the delayed phase transformation from β - to α -TCP promotes the sintering of the β -TCP powder and decreases the porosity. This is consistent with the obtained results. Therefore, it is concluded that the additives raise the transition temperature and this controls the phase and structure of the resultant materials.

On the other hand, the effect of the additives on the porosities and phases of samples was dependent on the natures of the additives. According to phase diagrams for the system $\text{Ca}_3(\text{PO}_4)_2$ - $\text{Mg}_3(\text{PO}_4)_2$ ¹⁰⁾ and $\text{Ca}_3(\text{PO}_4)_2$ - $\text{Zn}_3(\text{PO}_4)_2$ ¹¹⁾, the addition of Mg is more effective in increasing the transformation temperature from β - to α -TCP than that of Zn. Therefore, the addition of Mg significantly decreases porosity and increases the content of β -TCP phase compared to the addition of Zn. It is considered that the addition of Fe also increased the transition temperature as the case of the addition of Zn, since its effect on the porosity and phase content was similar to that of Zn. Moreover, the fact that we used not mol% but mass% should also have affected the different effectiveness of additives. The atomic weights of Mg, Fe and Zn are 24.31, 55.85 and 65.39, respectively. As the atomic weight of Mg is smaller than that of Fe or Zn, the mol% of Mg in the sample is greater at the same mass %. Therefore, the effect of magnesium might be greater than zinc or iron at the same mass %.

When the Mg content was 0.1 mass%, a porous body consisting of α - and β -TCP with continuous pores ranging from 10 to 50 μm could be prepared by the conventional sintering method without decreasing the porosity.

4 Conclusion

It was revealed that the porosity and phase of porous tricalcium phosphate can be controlled by addition of Mg, Fe and Zn. The addition of Mg was most effective to decrease the porosity and α -TCP content. When the Mg content was 0.1 mass%, a porous body consisting of α -TCP and β -TCP with continuous pores ranging from 10 to 50 μm could be prepared by the conventional sintering method.

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