CHARACTERIZATION AND HYDRATION REACTIVITY OF α -TRICALCIUM PHOSPHATE PREPARED BY HEATING WITH GYPSUM

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Abstract: Beta tricalcium phosphate (β -Ca₃(PO₄)₂, β -TCP) mixed with gypsum (CaSO₄·2H₂O) was heated at 1300°C and 1400°C. The resulting products were characterized by DTA, XRD, FTIR, EDX and hydration reactivity. An inhibition effect on the transition of the low temperature form β to high temperature form α was observed with increasing the amount of gypsum. The substitution of SO₄ for PO₄ was suggested from increases of the $\beta \rightarrow \alpha$ transition temperature and hydration reactivity. However both the substitution and the presence of S were not recognized by XRD, EDX and FTIR. Increasing the amount of gypsum resulted in the formation of hydroxyapatite (Ca₅(OH)(PO₄)₃) at 1300°C and tetracalcium phosphate (Ca₄(PO₄)₂O) at 1400°C. The hydration reactivity was in the order, pure α -TCP << α -TCP heated with gypsum.

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INTRODUCTION

Tricalcium phosphate (Ca₃(PO₄)₂, referred to as TCP) has two polymorphs named low temperature form β and high temperature form α . The transition temperature is *ca.* 1180°C. β -TCP ceramics is applied to artificial bone substitute. Whereas α -TCP powder is a basic material for making bone cements using its unique chemical property, *i.e.*, hydration-hardening. Powdery α -TCP is easily prepared by rapid cooling from temperatures above the transition temperature. On the other hand, the preparation of β -TCP bulk ceramics had a certain difficulty because temperatures for its sintering are generally required to be higher than the transition temperature. So, many studies on increasing the transition temperature have been done for producing β -TCP ceramics. For instance, the inhibiting effect of the substitution of Mg²⁺ and Al³⁺ for Ca²⁺ on the $\beta \rightarrow \alpha$ transition is well-known to be remarkable. The dissolving limit of Mg

into β -TCP have been reported to be around 13.6¹ in Mg/(Ca+Mg) mol% at 1000°C, and 13.2² at 1175°C. Hashimoto *et al.* clarified the conditions for the precipitation of whitlockite 6Ca₃(PO₄)₂ · 2MgHPO₄ from aqueous solution, and studied in detail on its heated product, *i.e.*, Mg-containing β -TCP^{3,4}. With the dissolution of Mg²⁺ into the β -TCP structure, the lattice constants became contracted, and the ν_3 stretching infrared spectroscopic (IR) bands assigned to PO₄ showed a blue-shift and splits due to a lowering of the symmetry of PO₄⁵.

On the other hand, chemical or structural influences of substitutions of anions for PO₄ have been also studied. Motisuke *et al.*⁶ prepared Si-doped α -TCP with a Si/(P+Si) mol% of 2.5 below 1200°C. The dissolution of AlPO₄ into TCP resulted in a remarkable chemical and structural stability of the β structure, and no transition into α -TCP even at 1300°C⁷. Toriyama *et al.*⁸ reported that the mixed dissolution of Al₂O₃ and SiO₂ into TCP

resulted in the β structure, *e.g.*, no transition at 1200°C, however the single dissolution of each of them did not stabilize the β structure. Barnes *et al.*⁹ reported that TCP-Ca₂SiO₄ solid solutions were hydrated to form a mixture of hydroxyapatite (Ca₅(OH)(PO₄)₃, Ap), C-S-H gel and Ca(OH)₂, however the hydration activities were lower than that of pure α -TCP. Berry *et al.*¹⁰ studied the reaction between gypsum (CaSO₄ · 2H₂O, G_{2H}) and brushite (CaHPO₄ · 2H₂O) by thermogravimetric (TG) analysis and clarified that the reaction producing β -TCP and SO₃ started at 800°C and completed at 950°C, however did not mention the dissolution of SO₄ into the β structure. Marraha *et al.*¹¹ reported the formation of SO₄-dissolving β -TCP. It was performed by heating a mixture of Ap and (NH₄)₂SO₄ at temperatures from 1000 to 1100 °C . The resulting β -TCP had IR absorption bands at 1150 and 1200 cm⁻¹, and no band at 674 cm⁻¹ of SO₄ in pure anhydrous gypsum (CaSO₄, II G) and no bands at 945 and 970 cm⁻¹ of PO₄ in pure β -TCP. Trombe *et al.*¹² reported also SO₄-substituted β -TCP with specific absorptions at 1150 and 1200 cm⁻¹, and without 674 cm⁻¹ of CaSO₄, 945 and 970 cm⁻¹ of pure β -TCP. The solid solution reaction and chemical composition were proposed by the reaction, $[Ca_{21}\square_3][(PO_4)_{14}\square_2] + 2CaSO_4 \rightarrow [Ca_{23}\square][(PO_4)_{14}(SO_4)_2]$ at 1000-1100 °C, where $\square$ is Ca-site vacancy existing originally in the β -TCP structure. Chabchoub *et al.*¹³ presented X-ray diffraction (XRD) and IR spectroscopic features of TCP-MSO₄ (M= Sr, Ba) solid solutions with the β -phase deficient compositions prepared at 1000 °C . Supposing the stoichiometric replacement of PO₄ by SO₄, Ca-site deficiencies could be introduced as follows:

When such a reaction does not occur, the following simple reactions are written.

In the present study, expecting the increases in hydration reactivity of TCP, synthetic β -TCP was heated with G_{2H} at high temperatures above 1200 °C . The resulting products were characterized in detail.

EXPERIMENTAL

The starting materials used were reagent grades of CaHPO₄ · 2H₂O, CaCO₃, and G_{2H}. The first two materials were weighed in the stoichiometric ratio of the TCP composition, then added with G_{2H} at 1-10 mass% corresponding to 1.8-18 mol% in G_{2H}/TCP ratio, then the mixtures were milled thoroughly using an agate mortar. Thus obtained mixtures were heated at 1300 °C (partially 1400 °C), then cooled rapidly to room temperature, and then ground to a degree of passing through a 150 inch-mesh sieve (BET surface area estimated : *ca.* 1.0 m²/g¹⁴). The resulting products were examined on the phase of TCP and whether or not SO₄ ions dissolved in the TCP structure by using DTA (MAC SCIENCE, TG-DTA2000s), XRD (MAC SCIENCE, M03X-HF), FTIR (JASCO, FTIR-230) and EDX (HORIBA, EMAX-5770). The hydration reactivity and hardening runs were carried out under conditions : 0.5 g powdery sample / 50 ml H₂O in a sealed vessel, 80°C, without stirring. The resulting products

sedimented in the bottom of the vessel were evaluated by XRD about reactivity and by touching the sediment by hand about hardening.

RESULTS AND DISCUSSION

DTA

When the solid-solution reaction of G_{2H} with TCP occurs as Eq. (1), the $\beta \rightarrow \alpha$ transition temperature must be influenced. FIGURE 1 shows DTA curves of β -TCP and a G_{2H} -added β -TCP. The $\beta \rightarrow \alpha$ temperature increased from 1198 to 1253 °C. In other words, a structural influence of G_{2H} on TCP was clear. The reversible endothermic and exothermic peaks around 1410-1430 °C assigned to the $\alpha \rightleftharpoons \alpha'$ transition was studied separately in detail by DTA and presented elsewhere¹⁵.

FIGURE 1 DTA curves of β -TCP (solid line) and 10mass% G_{2H} -added β -TCP (broken line). (25.0mg sample, 25 °C/min, in quiescent air)

Structural characterization of products

FIGURES 2 and 3 show XRD patterns and FTIR spectra of products quenched from 1300 °C in the system β -TCP- G_{2H} . The addition of G_{2H} tended to inhibit the $\beta \rightarrow \alpha$ transition, *i.e.*, suggested the partial substitution of SO_4 (ion radius 0.230 nm) for PO_4 (0.238 nm) as written by Eq. (1). However, no XRD peak shifts of reaction

products, *i.e.*, α -TCP, β -TCP, Ap and tetracalcium phosphate $Ca_4(PO_4)_2O$ within an experimental error. And also, in the FTIR spectra, any clear changes among heating products with and without G_{2H} , *e.g.*, splitting peaks (1150, 1200 cm^{-1}) observed in the spectrum of SO_4 -substituted β -TCP¹³, were not recognized.

FIGURE 2 XRD patterns of products in the system β -TCP- G_{2H} (1300 °C-3h, quenched) and references (pure β -TCP and II G (II $CaSO_4$) heated at 1300 °C for 3h. α : α -TCP, β : β -TCP, Ap: Hydroxyapatite

FIGURE 3 FTIR spectra of products in The system β -TCP- G_{2H} (1300 °C-3h, quenched) and references (β -TCP, II G).

In order to reconfirm such an inhibiting effect, an experiment using CaCO_3 instead of $\text{G}_{2\text{H}}$ was conducted. TABLE 1 summarized XRD phases of the resulting solid products at 1300°C and 1400°C . The difference between the products in the systems $\beta\text{-TCP-G}_{2\text{H}}$ and $\beta\text{-TCP-CaCO}_3$ with the same CaO mol% indicated the inhibition of $\text{G}_{2\text{H}}$ to the transition of TCP from β to α . The presence of element S was also checked by EDX (FIGURE 4), however not detected.

TABLE 1 XRD phase of products in the system $\beta\text{-TCP-G}_{2\text{H}}$.

G _{2H} + β -TCP mixture G _{2H} /mass% (mol%)	XRD phase ^{a)} after heating	
	1300°C-3h	1400°C-3h
0 (0)	αT	αT
1.0 (1.8)	αT	—
2.0 (3.6)	αT	—
4.0 (7.2)	$\alpha\text{T} > \beta\text{T, Ap}$	—
5.0 (9.0)	$\alpha\text{T} > \text{Ap} > \beta\text{T}$	$\alpha\text{T} > \text{Te}$
6.0 (10.8)	$\alpha\text{T, } \beta\text{T, Ap}$	$\alpha\text{T} > \text{Te}$
10.0 (18.0)	$\beta\text{T} > \text{Ap}$	$\alpha\text{T, } \beta\text{T} > \text{Te}$
5.8 ^{b)} (18.0)	$\alpha\text{T, Ap}$	—

- a) βT : β -TCP, αT : α -TCP, Ap:Hydroxyapatite,
Te: Tetracalcium phosphate ($\text{Ca}_4(\text{PO}_4)_2\text{O}$)
b) CaCO_3 was added instead of $\text{G}_{2\text{H}}$.

Consequently, the substitution itself of SO_4 for PO_4 could not directly detected, however the DTA curves showed clearly a structural influence suggesting the substitution.

Hydration reactivity

FIGURE 5 shows XRD patterns of products after the hydration run, and TABLE 2 summarized changes of the products. Formation degrees of Ap, which reflects the hydration reactivity, were in the order, pure α -TCP $\ll$ α -TCP heated with $\text{G}_{2\text{H}}$. This result suggested also the substitution of SO_4 for PO_4 as well as the above DTA

FIGURE 4 EDX spectra of products in the system $\beta\text{-TCP-G}_{2\text{H}}$ (1300°C -3h, quenched).

FIGURE 5 XRD patterns of products in the system $\beta\text{-TCP-G}_{2\text{H}}$ (1300°C -3h, quenched) after the hydration run (80°C -1h, without stirring).

α : α -TCP, β : β -TCP, A:Hydroxyapatite

TABLE 2 Hydration reactivity and hardening of products in the system β -TCP- G_{2H} .

β -TCP+ G_{2H} mixture G_{2H} /mass% (mol%)	Prepared products (1300°C-3h)	Hydration in H_2O at 80°C without stirring (0.5g/50ml)			
		After 1h		After 3h	
	XRD ^{a)}	Hardening	XRD ^{a)}	Hardening	XRD ^{a)}
0 (0)	α T	X	α T	X	α T
1.0 (1.8)	α T	O	α T >> Ap	O	Ap >> β T, α T
2.0 (3.6)	α T	O	α T, Ap	O	Ap >> β T
3.0 (5.4)	α T >>> β T	O	Ap, α T > β T	---	---
4.0 (7.2)	α T >> β T, Ap	O	Ap > α T > β T	---	---
5.0 (9.0)	α T > Ap > β T	O	Ap > α T > β T	O	Ap >> α T > β T
6.0 (10.8)	α T, β T > Ap	O	β T > Ap, α T	---	---
10.0 (18.0)	β T > Ap	X	β T > Ap	X	β T > Ap

a) β T: β -TCP, α T: α -TCP, Ap: Hydroxyapatite

CONCLUSIONS

The addition of gypsum ($CaSO_4 \cdot 2H_2O$) to tricalcium phosphate ($Ca_3(PO_4)_2$, TCP) tended to inhibit the transition of the low temperature form β to the high temperature form α of TCP. However both the substitution of SO_4 for PO_4 and the presence of S were not detected directly. Increasing the amount of gypsum resulted in the formation of hydroxyapatite ($Ca_5(OH)(PO_4)_3$) at 1300°C and tetracalcium phosphate ($Ca_4(PO_4)_2O$) at 1400 °C. The hydration reactivity of α -TCP prepared at 1300°C was in the order, pure α -TCP << α -TCP heated with G_{2H} .

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