HYDRATION-HARDENING PROPERTIES OF DIVALENT CATION-SUBSTITUTED α -TRICALCIUM PHOSPHATE

Hideki Monma^{1*}, Yuji Hosoi², Toshinori Okura², Hironori Ogata¹,

Yusuke Moriyoshi¹

(*Corresponding author: monma@cc.kogakuin.ac.jp)

¹Research Center for Micro-Nano Technology, Hosei University,
3-11-15 Midori-cho, Koganei-shi, Tokyo 184-0003, Japan

²Faculty of Engineering, Kogakuin University,
2665 Nakano-cho, Hachioji-shi, Tokyo 192-0015, Japan

Keywords: Tricalcium phosphate, Hydroxyapatite, Hydration activity, Hydration-hardening,

Abstract: Divalent cation-substituted α -phase tricalcium phosphates (α -Ca_{3-x}M_x(PO₄)₂, where M = Mg, Zn, Sr, Ba) were obtained by heating at 1500°C for M=Mg ($x = 0.03$), 1400°C for the others ($x = 0.09$), respectively. The resulting products were characterized by XRD, hydration reactivity and hydration-hardening strength. The hydration reactivity of these α -phase phosphates was decreased by the substitutions, regardless of smaller or larger M in ion size than Ca, *i.e.*, the α phase was chemically stabilized.

(Received May 19, 2010; Accepted July 31, 2010)

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. Sintered β -TCP is applied to artificial bone substitute. Whereas powdery α -TCP having a unique hydration-hardening property is a basic material for artificial bone cements. In the sintering of β -TCP, higher temperatures than the transition temperature were generally required. So, many studies on increasing the transition temperature have been done through the substitution of various kinds of cations for Ca²⁺. For instance, the substitutions of Al³⁺ and Mg²⁺ resulted in a remarkable chemical and structural stability of the β structure, *e.g.*, no transition into α -TCP occurred even at 1300°C^{1,2)}. Observed lattice contracts of the β structure were discussed in relation to the differences in ion radius among Al³⁺ (0.057 nm), Mg²⁺ (0.072 nm) and Ca²⁺ (0.100 nm). On the other hand, α -TCP is easily prepared

by rapid cooling from temperatures above the transition temperature, however basic and crystal chemical studies such as studies on β -TCP have been a little. Motisuke *et al.*³⁾ prepared Si-doped α -TCP with a Si/(P+Si) mol% of 2.5 below 1200°C. Barnes *et al.*⁴⁾ reported that quenched products from 1500°C in the system TCP-Ca₂SiO₄ hydrated to form a mixture of hydroxyapatite (HAP, stoichiometrically Ca₅(OH)(PO₄)₃), C-S-H gel and Ca(OH)₂, however the hydration activities of quenched products were lower than that of pure α -TCP. At present, controlling or increasing the hydration and hardening properties of α -TCP has become of interest in the fields of biomaterials.

In the present work, the influence of the substitution of divalent cations for Ca²⁺ in α -TCP on the hydration-hardening properties was investigated. The cations were Mg²⁺ (0.072 nm), Zn²⁺ (0.075 nm), Sr²⁺ (0.116 nm) and Ba²⁺ (0.136 nm) which are smaller or larger ions in size than Ca²⁺.

EXPERIMENTAL

Stoichiometric mixtures with 1.50 in (Ca+M) / P molar ratio (M = Ca, Mg, Zn, Sr, Ba) were prepared using reagent grades of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 , MgO , ZnO , SrO and BaO . Mixing molar ratios in M / (Ca+M) were 0.00 for Ca, 0.01 for Mg and 0.03 for the others. The mixtures were milled for 3 h using an automatic alumina mortar. Thus obtained mixtures were heated two times at 1000°C for 3 h, then heated for 3 h at 1300°C for pure α -TCP (M=Ca), at 1500°C for M = Mg, at 1400°C for M = Zn, Sr and Ba, and then cooled rapidly to room temperature. The resulting products written as $\text{Ca}_{2.97}\text{Mg}_{0.03}(\text{PO}_4)_2$ and $\text{Ca}_{2.91}\text{M}_{0.09}(\text{PO}_4)_2$; M = Zn, Sr, Ba were confirmed to have the α single phase by XRD (MAC SCIENCE, M03X-HF, $\text{CuK}\alpha$ -radiation, 40 kv-15 mA, slits:1- 1-0.15, scan speed: $2^\circ/\text{min}$). The hydration reactivity was evaluated by qualitative observation of appeared XRD peaks of HAP and of hardening or non-hardening of the powder sediment after the hydration run (1.0 g powder sample / 50 ml H_2O , at 80°C for 1 h, without stirring). After the preliminary observation with XRD and SEM (HITACHI, Model S-2380N)) on hydration-hardening, prepared α -phase TCP powders were ground and passed through 150-mesh sieve. Then slurries with H_2O at Powder/Liquid=1.67 g/g were poured into a brass mold with 10x10x80 mm, wrapped with a commercial plastic thin film, then warmed at 80°C for 3 h. Thus obtained products were demolded, dried at 40°C for 24 h, then cut into specimens with 10x10x25 mm for the compressive strength test. Compressive strength was measured at a cross-head speed of 2.5 mm / min by using a mechanical testing apparatus (SHIMADZU, Autograph AG-10KNI). Porosities of hardened products were

measured by the Archimedes method using H_2O as a dipping liquid.

RESULTS AND DISCUSSION

FIGURE 1 shows XRD patterns of products quenched from 1500°C for M = Mg and from 1400°C for the other M. All of products were the single α -phase of TCP. Peak shifts due to the substitution of M ions for Ca ion in α -TCP were not clear, however the following difference in hydration reactivity suggested the substitutions of M.

FIGURE 1 XRD patterns of α -TCP and $\text{Ca}_{3-x}\text{M}_x(\text{PO}_4)_2$.

●: α -phase of TCP

FIGURE 2 shows XRD patterns of products after the hydration runs for pure α -TCP and α - $\text{Ca}_{3-x}\text{M}_x(\text{PO}_4)_2$ at 80°C for 1 h. Pure α -TCP and Sr-substituted α -TCP formed HAP with fairly amounts, however the case of Ba was a small, and the cases of Mg and Zn were non-changed. Although the resulting products with a lattice strain introduced by the substitutions for Ca were expected to be higher than pure α -TCP in chemical reactivity, actually structural shrinkage or residual

lattice strain seemed to chemically strengthen the α -structure. The composition of the HAp must be nonstoichiometric, *i.e.*, $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x} \cdot n\text{H}_2\text{O}$; $0 < x \leq 1$.

FIGURE 2 XRD patterns of α -TCP and α - $\text{Ca}_{3-x}\text{M}_x(\text{PO}_4)_2$ after the hydration run at 80°C for 1 h.

●: α -phase of TCP A: HAp

TABLE 1 summarized the above results on α - $\text{Ca}_{3-x}\text{M}_x(\text{PO}_4)_2$ compared to α -TCP. FIGURE 3 shows SEM microstructures before and after the hydration runs of α -phase TCP samples. In the case of α -TCP, characteristic thin leaves of nonstoichiometric HAp were clearly observed.

TABLE 1 Characteristics of α - $\text{Ca}_{3-x}\text{M}_x(\text{PO}_4)_2$

M		Mg	Zn	Ca	Sr	Ba
Ion radius nm		0.072	0.075	0.100	0.116	0.136
x		0.03	0.09	0.00	0.09	0.09
XRD phase*		α	α	α	α	α
Hydration (1g 50mlH ₂ O, 80°C-1h)	XRD phase*	α	α	$\alpha + \alpha$	$\alpha > \alpha$	$\alpha > \alpha > \alpha$
	Hardening of sediment	None	None	Yes	Yes	None

* α : α -phase of TCP. A: HAp

FIGURE 3 SEM photographs of α - $\text{Ca}_{3-x}\text{M}_x(\text{PO}_4)_2$ before and after the hydration run at 80°C for 1 h. Bar: $5\mu\text{m}$

Consequently, regardless of the ion size of the cations substituted for Ca in α -TCP, the hydration reactivity of α -TCP was decreased by the substitutions at impurity levels. Figure 4 shows a hardened specimen cut for compressive strength test. Figure 5 shows plots of compressive strength vs. porosity of thus obtained hardened bodies with literature data. It was considered that the plots for

FIGURE 4 Specimen (10x10x25mm) for compressive strength test.

FIGURE 5 Plots of compressive strength (σ_c) vs. porosity (p) of hardened bodies prepared at 80°C for 3 h from α -TCP ($\odot$) and α -Ca_{3-x}M_x(PO₄)₂ ($\triangle$, ∇ , $\square$, $\diamond$).

$\circ$: α -TCP+CaHPO₄·2H₂O+ascorbic acid cement slurry, centrifugal sediment hardened at 40°C-3h⁵⁾

$\bullet$: α -TCP cement paste, hardened at 80°C-3h⁶⁾

hardened bodies from paste (this work) were reasonable compared to those for centrifugal sediment⁵⁾ and spontaneous sediment⁶⁾.

CONCLUSIONS

Divalent cation-substituted α -tricalcium phosphates (α -Ca_{3-x}M_x(PO₄)₂, where M = Mg, Zn, Sr, Ba) were prepared and characterized by XRD, SEM, hydration reactivity and hardening strength. The hydration reactivity of pure α -TCP was decreased by the substitutions of either smaller or larger cations in size than Ca. In other words, such divalent substitutions tended to stabilize the α -TCP structure.

REFERENCES

1. H.Monma, T.Kanazawa, *Yogyo-Kyokai-Shi*, **86**, 378(1978).
2. K.Yoshida, H.Hyuga, N.Kondo, H.Kita, M. Sasaki, M.Mitamura, K.Hashimoto, Y.Toda, *J. Amer. Ceram. Soc.*, **89**, 688(2006).
3. M.Motisuke, R.G.Carrodegua, C.A.C. Zavaglia, *Key Eng. Mater.*, **361-363**, 199(2008).
4. M.W.Barnes, M.Klimkiewicz, P.W.Brown, *J. Amer. Ceram. Soc.*, **75**, 1423(1992).
5. H.Monma, Unpublished data.
6. H.Monma, S.Ueno, M.Tsutsumi, *Gypsum & Lime*, No.156, 6(1978).