Liquid Infiltration of Porous Calcium Hydroxide Solid for Synthesizing Bulk Calcium Phosphate Biomaterials

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Abstract Bulk calcium phosphate biomaterials without sintering were synthesized at room temperature by infiltrating various orthophosphate aqueous solutions into a porous Ca(OH)_2 green powder compact. These orthophosphate aqueous solutions were prepared from a different ratio of $\text{Ca(OH)}_2/\text{H}_3\text{PO}_4$ up to $\text{pH}=12$. The infiltrated specimens did not show any shape or dimension changes at a lower concentration of H_3PO_4 or a liquid with $\text{pH}>2$. When the liquid contained some supersaturated solids or precipitates, the infiltrated specimens showed their reacted phases at the surface similar to these supersaturated precipitates, which were $\text{Ca(H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (MCPM), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (DCPD), or $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HA) as pH was increasing. Under a liquid infiltration with a lower concentration of H_3PO_4 liquid, a functional graded calcium orthophosphate composite was observed. Furthermore, relationships among processing factors like pH plus impurities and liquid concentration, phase formation, and microstructure of infiltrated specimens were discussed in detail.

Keywords Calcium Phosphate, Liquid Infiltration, Reaction Formation, Biomaterial

phases [1,8-12]. However, not every orthophosphate is already being well-defined in its formation; therefore, some of these orthophosphate phases are still under investigation.

Based on the previous findings, different calcium orthophosphate powders are very easy to obtain in the $\text{Ca(OH)}_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ ternary system. In this study, we will use an alternative way to prepare a bulk calcium orthophosphate composite instead of a powder form. This is because a chunk of reacted or unreacted Ca(OH)_2 solid form is frequently found if the $\text{Ca(OH)}_2/\text{H}_3\text{PO}_4$ aqueous solution is not well mixed [7]. Even though this phenomenon is a shortcoming for powder preparation, but it may be a convenient way to obtain a bulk calcium phosphate composite at room temperature. Therefore, a porous Ca(OH)_2 green powder compact is designed to infiltrate the supersaturated orthophosphate aqueous solution, in which phosphate ions such as H_2PO_4^- , HPO_4^{2-} , or PO_4^{3-} are phase equilibrated or coexist with their related calcium orthophosphates. It is hoped that a bulk porous calcium phosphate composite is obtained through this liquid infiltration method for orthopedic or other related applications. Furthermore, phases and microstructures of infiltrated specimens are also observed to explain the possible reaction mechanisms of this liquid infiltration.

1. Introduction

A ternary system $\text{Ca(OH)}_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ has been extensively studied for preparing calcium orthophosphate materials, especially in powder fabrication [1-7]. In the aqueous solution, most calcium orthophosphates being observed are MCPM (monocalcium phosphate monohydrate, $\text{Ca(H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$), DCPD (dicalcium phosphate dihydrate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), and HA (hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) etc., which are dependent of pH, concentration of ions Ca^{2+} , and P^{5+} or PO_4^{3-} during the processes. Some other orthophosphates, such as OCP (octacalcium phosphate, $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4\text{5H}_2\text{O}$) and CDHA (calcium-deficient hydroxyapatite, $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$, $0 < x < 1$), are believed to be intermediate, metastable, or other derivative

2. Materials and Methods

Starting chemicals were Ca(OH)_2 (95% pure, Nippon Shiyaku Kogyo K.K., Osaka, Japan), H_3PO_4 (85% pure, Union Chemical Work LTD, Hsinchu, Taiwan), NH_4OH (28% pure, Nippon Shiyaku Kogyo K.K., Osaka, Japan). These starting chemicals were used to prepare a porous Ca(OH)_2 green powder compact or a specific type of orthophosphate aqueous solution up to $\text{pH}=12$.

2.1. Preparations of Porous Ca(OH)_2 Green Powder Compacts and Orthophosphate Aqueous Solutions

A porous Ca(OH)_2 green powder compact, with the cylindrical dimension of $\phi 1.2\text{cm}$ (D) $\times$ $\sim 0.3\text{cm}$ (T) (D,

diameter; T, thickness), was formed from a batch of 0.5g $\text{Ca}(\text{OH})_2$ initial powder inside a cylindrical stainless steel die under a uniaxial compressive stress up to 22Kg/cm^2 , to obtain a porosity up to 30vol%.

As to a specific orthophosphate aqueous solution at a different pH up to pH=12, it was obtained from the different portions of $\text{Ca}(\text{OH})_2$ and 0.06M or 1.2M H_3PO_4 , as listed in Table 1, by mixing and also staying-put over a day to observe any pH change. The pH values of these orthophosphate aqueous solutions were measured by using a pH meter (PHM 210 Standard pH Meter, Radiometer Analytical SAS, Villeurbanne Cedex, France).

Table 1. Different orthophosphate solutions for liquid infiltration

orthophosphate solution	H_3PO_4 (ml)		$\text{Ca}(\text{OH})_2$ (g)	pH
	1.2M	0.06M		
LP		100	0.0	1.89
LP2		100	0.040	2
LP4		100	0.225	4
LP6		100	0.44	6
LP8		100	0.47	8
LP10		100	0.51	10
LP12		100	0.58	12
HP	100.0		0.0	1.03
HP2	165.0		5.0	2
HP4	55.5		5.0	4
HP6	37.5		5.0	6
HP8	35.0		5.0	8
HP10	33.5		5.0	10
HP12	28.0		5.0	12

2.2. Liquid Infiltration

A 0.5g $\text{Ca}(\text{OH})_2$ green powder compact was submerged into a specific orthophosphate solution at room temperature for 1h up to 1 week to observe its liquid infiltration phenomena and pH changes. From preliminarily observations, there were no any significant pH changes before and after liquid infiltration.

2.3. Phase Determination and Microstructure Observations

Phase existence of infiltrated samples or initial powders were determined from X-ray diffraction patterns (XRDs) at room temperature by using an X-ray unit (X'Pert PRO, PANalytical Inc., Netherlands) at $2\theta=20-80^\circ$, with a scanning speed of $3^\circ/\text{min}$ and a sampling interval of $\Delta\theta=0.04^\circ$. For microstructure observations, a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi Inc., Germany) was used to observe the free surface or fracture surface of infiltrated specimen.

3. Results

3.1. Macrographs and phase existence of liquid infiltrated specimens.

Macrographs of liquid infiltrated specimens are shown in Fig. 1. From these optical macrographs, the $\text{Ca}(\text{OH})_2$ powder compact is completely dissolved in the HP solution, but slightly dissolved in the HP2 solution because its dimension is a little smaller than the original, as shown in Fig. 1. Therefore, $\text{Ca}(\text{OH})_2$ powder compacts are very easy to dissolve in the higher concentrated H_3PO_4 , but not in the lower concentration of H_3PO_4 . However, the rest samples at higher pHs do not show any significant dimension changes. It indicates that the transformed phases inside the infiltrated specimen can be bonded together without any significant dimension change, even though the initial $\text{Ca}(\text{OH})_2$ powder compact is simply mechanically-bonded.

Figure 1. Optical macrographs of infiltrated $\text{Ca}(\text{OH})_2$ specimens after being treated in different orthophosphate solutions HP-HP12 and LP-LP12.

Figure 2. X-ray diffraction patterns at the surfaces of infiltrated specimens (a) LP, (b) LP4, (c) LP10, (d) MCPM (JCPDS 09-0347), (e) DCPD (JCPDS 09-0077), (f) HA (JCPDS 09-0432). Symbols "1", "2", and "3" are for MCPM, DCPD, and HA, respectively.

X-ray diffraction patterns (XRDs) at the surface of the infiltrated specimens are selectively shown in Fig. 2. From these XRDs, phases at the infiltrated surfaces are MCPM, DCPD, and HA as the pH value of infiltrated aqueous solution increases. MCPM exists in the infiltrated specimen LP; DCPD is present in the infiltrated specimens HP2-HP6 and LP2-LP6. However, HA is formed in the infiltrated

specimens HP8-HP12 and LP8-LP12. There are no any trace of $\text{Ca}(\text{OH})_2$ X-ray diffraction peaks being observed on the surface of these infiltrated specimens. Therefore, the initial $\text{Ca}(\text{OH})_2$ powder on the surface is already completely transformed into new calcium orthophosphate phases after liquid infiltration.

Figure 3. SEM micrographs at the surfaces of infiltrated specimens (a)LP, (b)LP2, (c)LP4, (d)LP12, (e)HP2, and (f)HP10.

3.2. Microstructures of Liquid-infiltrated Specimens

(a) Microstructures on the infiltrated surface.

SEM micrographs of infiltrated specimens at the surface are representatively shown in Fig. 3. It indicates that calcium orthophosphates grow faster at a low pH value. This phenomenon also can be seen from the corresponding X-ray diffraction patterns, as shown in Fig. 2. Calcium hydroxyapatite (HA) crystals shown in Fig. 2(c) have much broader diffraction peaks, which demonstrate HA having much smaller grains or domains, if compared with Figs. 2(a) & 2(b). At lower pHs, calcium orthophosphates are plate-like for MCPM and DCPD. However, at higher pHs, HA seems shows ellipsoid-like morphologies.

(b) Fractographs perpendicular to the infiltration surface.

In the LP solution ($\text{Ca}(\text{OH})_2/0.06\text{MH}_3\text{PO}_4$ system), a fractograph of infiltrated specimen perpendicular to the free surface is shown in Fig. 4(a). Free surface or the infiltrated surface contains several large holes, which were produced

from the chemical reaction between the $\text{Ca}(\text{OH})_2$ powders and H_3PO_4 , but not from the original pores. Except for the free surface, several different fracture morphologies, upper area, transition zone, plus lower area in the reacted zone, and unreacted zone are defined in this fractograph. This is because these areas have different contents of Ca, P, and O elements, as shown in Figs. 4(b), (c), & (d). Based on the trace content of P, the unreacted zone is identified to be the location of the original $\text{Ca}(\text{OH})_2$ powders, which are not being liquid infiltrated. As to the reacted zone, the upper area has a higher P content, but a lower Ca content if compared it with the lower area.

Figure 4. (a) A fractograph perpendicular to the free surface of infiltrated specimen LP, and its EDXS in the (b) upper area, (c) lower area, and (d) unreacted zone.

Figure 5. A schematic diagram of solid/liquid interface in the liquid infiltration front.

4. Discussion

4.1. Liquid Infiltration

In the $\text{Ca(OH)}_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ system, phase existence is correlated with pH, temperature, and concentration of Ca^{2+} , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} [3,5,6,13]. As to the liquid infiltration of $\text{Ca(OH)}_2/\text{H}_3\text{PO}_4$ in this study, phase formation mechanisms in the infiltrated Ca(OH)_2 specimen are discussed as follows.

(a) Liquids with a low pH value without any supersaturated precipitates

Infiltrated liquids such as HP, HP2, LP, and LP2 do not contain any apparent supersaturated precipitates; therefore, when a porous Ca(OH)_2 green powder compact are put inside these liquids, these liquids are expected to react with Ca(OH)_2 instantaneously. This is because Ca(OH)_2 is not a stable phase in a low pH aqueous solution. The dissolution rate of Ca(OH)_2 is dependent of its solubility product (K_{sp}) and the formation mechanisms of a new calcium orthophosphate phase, in which $K_{sp} = (\text{Ca}^{2+})_{aq}(\text{OH}^-)_{aq}^2$, $(\text{Ca}^{2+})_{aq}$ and $(\text{OH}^-)_{aq}$ are the concentrations of Ca^{2+} and OH^- in the aqueous solution (aq), respectively.

From solubility product (K_{sp}), when a Ca(OH)_2 powder compact is impregnated in a low pH solution or a not supersaturated solution, such as a H_3PO_4 solution (LP or HP liquid), $(\text{OH}^-)_{aq}$ is very low; subsequently for maintaining a constant K_{sp} , more Ca(OH)_2 powders should be dissolved to increase $(\text{Ca}^{2+})_{aq}$. From the pH value listed in Table 1, the $\text{Ca(OH)}_2/0.06\text{M H}_3\text{PO}_4$ system (LP liquid) has a higher $\text{pH}=1.89$, or a higher concentration of OH^- than the $\text{Ca(OH)}_2/1.2\text{M H}_3\text{PO}_4$ system (HP liquid) with an $\text{pH}=1.03$; therefore, the dissolution rate in the HP liquid is expected to be faster than that in the LP liquid. As the dissolution of Ca(OH)_2 proceeds, $(\text{Ca}^{2+})_{aq}$ and $(\text{OH}^-)_{aq}$ are increasing. Consequently a new equilibrium state of $\text{H}_3\text{PO}_4 \leftrightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$ reaches at the $\text{pKa}=2.12$ in the liquid, and new calcium orthophosphate crystals or precipitates will appear at the solid/liquid interface, in which the solid is the porous Ca(OH)_2 powder compact. After reaching such conditions, except for K_{sp} , the dissolution rate of Ca(OH)_2 is also dependent of the formation mechanisms of these new calcium orthophosphate precipitates.

For an HP/ Ca(OH)_2 system, if a 0.5g Ca(OH)_2 powder compact is impregnated in a 100cc HP liquid, it will be completely dissolved in the liquid, as shown in Fig. 1. This is because a new equilibrium state $\text{H}_3\text{PO}_4 \leftrightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$ at $\text{pKa}=2.12$ does not reach yet, which can be seen from the amount of Ca(OH)_2 powder dissolution of liquid HP to HP2 as listed in Table 1. From liquid HP to HP2, the amount of Ca(OH)_2 dissolution is 5g in 165.0cc of 1.2M H_3PO_4 to reach $\text{pH}=2$; therefore, a complete dissolution of a 0.5g Ca(OH)_2 green powder compact in 100cc of 1.2M H_3PO_4 should not be able to obtain an $\text{pH}=2$. As to the HP2/ Ca(OH)_2 system, some Ca(OH)_2 powders are found to dissolve in the HP2 liquid, before reaching an equilibrium state $\text{H}_3\text{PO}_4 \leftrightarrow$

$\text{H}^+ + \text{H}_2\text{PO}_4^-$ or the infrastructure of MCPM ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) to replace the backbone structure of Ca(OH)_2 powders. Therefore, the infiltrated Ca(OH)_2 specimen HP2 shows some dimension changes in Fig. 1. However, in the LP/ Ca(OH)_2 and LP2/ Ca(OH)_2 systems, LP and LP2 liquids only need a slight amount of Ca(OH)_2 being dissolved in a 100cc liquid to reach a higher pH, as listed in Table 1; therefore, the infiltrated Ca(OH)_2 powder compacts don't show any apparent dimension changes in Fig. 1.

(b) Liquids with supersaturated precipitates

If an infiltrated liquid reaches the first equilibrium state of $\text{H}_3\text{PO}_4 \leftrightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$, during liquid infiltration, the infiltration front in the solid/liquid interface (solid for the porous Ca(OH)_2 powder compact) can be schematically described in Fig. 5. As the liquid infiltration proceeds, Ca^{2+} and OH^- ions are released to the solid/liquid interface due to the dissolution of the solid phase Ca(OH)_2 . The dissolution rate of Ca(OH)_2 is initially dependent of pHs. However, the OH^- ion release is not large enough to locally change the pH value of infiltrated liquid at the initial interface of $\text{Ca(OH)}_2/\text{liquid}$. Therefore, precipitates are formed from the reactions between Ca^{2+} from dissolution of Ca(OH)_2 and an orthophosphate ion H_2PO_4^- from the incoming infiltrated liquid. Subsequently, the phases of infiltrated specimen at the surface are the same crystal structures as the solid or precipitates in the original supersaturated aqueous solution. Therefore, MCPM, DCPD, and HA appear at the surface of infiltrated specimens as pH increases. Overall, the chemical reactions between Ca(OH)_2 and infiltrated liquid are classified to have three mechanisms: dissolution of Ca(OH)_2 , precipitation, and growth of new precipitates.

Among these three mechanisms for the chemical reactions of $\text{Ca(OH)}_2/\text{liquid}$ mentioned above, the most important factor for a successful liquid infiltration is preliminarily related to the dissolution rate of Ca(OH)_2 powders. As a result, for obtaining an intact infiltrated specimen, the dissolution rate of Ca(OH)_2 powders should keep as low as possible, especially at a low pH liquid.

(c) Functional graded materials

For a low pH liquid infiltration, if a porous Ca(OH)_2 can be continuously infiltrated with the supersaturated liquid, the reacted phases along the infiltration direction or in the thickness direction can be proposed as shown in Fig. 6. This layer-like microstructure is much easier to form under a lower phosphate concentration, because a smaller amount of Ca(OH)_2 dissolution can cause a higher pH change, as listed in Table 1.

At the first stage of liquid infiltration, an equilibrium state $\text{H}_3\text{PO}_4 \leftrightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$ of the infiltrated liquid can be reached at $\text{pKa}=2.12$. Therefore, MCPM starts to appear in zone I shown in Fig. 6. As the liquid infiltration proceeds, more Ca(OH)_2 reacts with the incoming infiltrated liquid from the open pore channels to increase its pH up to another equilibrium state of $\text{H}_2\text{PO}_4^- \leftrightarrow \text{H}^+ + \text{HPO}_4^{2-}$ at $\text{pKa}=7.21$, and then DCPD begins to form in the zone II. As the liquid is

further infiltrated into the porous $\text{Ca}(\text{OH})_2$ powder compact, the reacted infiltration liquid finally reaches to the other equilibrium state of $\text{HPO}_4^{2-} \leftrightarrow \text{H}^+ + \text{PO}_4^{3-}$ at $\text{pK}_a=11.77$, and HA is supposed to finally exist in zone III even if the intermediate phase such as OCP ($\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$) or CDHA ($\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$, $0 < x < 1$) is probably formed in the early transformation period.[1, 8-12]

Figure 6. Proposed layer structures along the infiltration direction for a specimen being liquid infiltrated in a low concentration of H_3PO_4 solution.

Microstructures shown in Fig. 4 contain three different morphologies along the thickness direction in the fractographs of the infiltrated specimen LP, upper area and lower area in the reacted zone, and unreacted zone. In this LP/ $\text{Ca}(\text{OH})_2$ system, the upper area (zone I) has been identified as MCPM from the corresponding XRD shown in Fig. 2(a). As to the lower area (zone II), it is DCPD because a lower content of P but a higher content of Ca is determined from EDXSSs shown in Figs. 4(b)-(d), by comparing it with the upper area (zone I). Except for EDXSSs, an XRD for an infiltrated specimen at a higher $\text{pH}=4$ (in the LP4 solution) also shows DCPD crystal structure at the infiltrated surface, as shown in Fig. 2(b). If the liquid can infiltrate further inside the $\text{Ca}(\text{OH})_2$ powder compact, HA or zone III can be obtained. Therefore, we believe a liquid infiltration method in the $\text{Ca}(\text{OH})_2/\text{H}_3\text{PO}_4$ can be used to fabricate a layer-like structure or a functional graded material.

4.2. Correlations between Liquid Infiltration and Vapor Infiltration

From SEM micrographs shown in Figs. 7(a), whisker morphologies are frequently being observed in the interface between the reacted and unreacted zones. This is because the chemical reaction between $\text{Ca}(\text{OH})_2$ and orthophosphate acid is an exothermic reaction during a liquid infiltration. For example, MCPM ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) is formed by the following chemical reaction:

which occurs exothermically at low pH aqueous solution, $\text{pH}<2$ [5,6,14,15]. This exothermic reaction will locally heat up the surrounding liquids and materials. In the reaction front, the interface between the reacted zone (in the

infiltrated liquid) and unreacted zone ($\text{Ca}(\text{OH})_2$ powders), some infiltrated liquids (or orthophosphate solutions) become vapors to vapor infiltrate into the unreacted $\text{Ca}(\text{OH})_2$ powders. Therefore, in the system of $\text{Ca}(\text{OH})_2$ powder and H_3PO_4 liquid, some whiskers have been found in the reaction front, interface between the reacted zone and unreacted $\text{Ca}(\text{OH})_2$ zone, as shown in Fig. 7(a). From EDXS in Fig. 7(b), these whiskers contain Ca, P, and O elements; however, their morphologies are different from calcium orthophosphates in the liquid infiltration. The same whisker morphologies have been reported in some calcium orthophosphates being obtained from a chemical vapor deposition [16]. Therefore, it is believed that these whiskers are formed from a vapor reaction. While the infiltrated liquid reaches, these whiskers are expected to react with the liquid to transform into another phase, except for the area of closed pores. As a result, whiskers are difficult to find inside the reacted zone after liquid infiltration.

Figure 7. (a) Whiskers formed in the interface between the reacted and unreacted zones, and (b) its corresponding EDXS.

4.3. Time Effect of $\text{Ca}(\text{OH})_2$ Green Powder Compact in the Air

If $\text{Ca}(\text{OH})_2$ green powder compacts are put in the air for a period of time, some of $\text{Ca}(\text{OH})_2$ powders are transformed into the CaCO_3 phase, as shown in Fig. 8(b). This is because $\text{Ca}(\text{OH})_2$ can absorb CO_2 from the environment to transform into CaCO_3 . From the comparisons of phase existence shown in Figs. 8(a)-8(b), it indicates that CaCO_3 in the initial

powders is a minor phase, but it becomes a major phase after these $\text{Ca}(\text{OH})_2$ green powder compacts have been left in the air for a week. During a higher pH orthophosphate liquid infiltration, CaCO_3 remains inside the infiltrated specimen and it is not transformed into any calcium orthophosphate phase, as shown in Fig.8(c). From X-ray diffraction patterns in Figs.8(b)-8(c), it shows that hydroxyapatite (HA) is from $\text{Ca}(\text{OH})_2$ not from $\text{Ca}(\text{CO}_3)_2$. However, $\text{Ca}(\text{CO}_3)_2$ can be dissolved in a very low pH orthophosphate liquid; therefore, it does not remain in the liquid infiltrated specimens.

Figure 8. X-ray diffraction patterns for (a) the initial $\text{Ca}(\text{OH})_2$ green compact, (b) a $\text{Ca}(\text{OH})_2$ green compact in the air for a week, (c) the CaCO_3 -containing $\text{Ca}(\text{OH})_2$ green compact after the liquid infiltration at pH=12, (d) $\text{Ca}(\text{OH})_2$ (JCPDS 72-0156), (e) CaCO_3 (JCPDS 05-0586), (f) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HA, JCPDS 09-432). Symbols “●” are for $\text{Ca}(\text{OH})_2$, “△” for CaCO_3 , and “◆” for HA.

5. Conclusions

Several aqueous solutions with a different ratio of $\text{Ca}(\text{OH})_2/\text{H}_3\text{PO}_4$ were designed to infiltrate into the $\text{Ca}(\text{OH})_2$ green powder compacts from pH=1 to pH=12. An intact shape of bulk infiltrated specimen was obtained without any significant dimension or shape changes when a low concentration of H_3PO_4 or a liquid with pH>2 was used.

Upon an infiltrated aqueous solution with the supersaturated calcium orthophosphate solids or precipitates, the infiltrated specimens showed their reacted phases at the surface similar to these supersaturated precipitates, which were MCPM ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) to DCPD($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), and further to $\text{HA}(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)$ as pH was increasing.

With a continuing liquid infiltration in the $\text{Ca}(\text{OH})_2/0.06\text{MH}_3\text{PO}_4$ system, the infiltrated specimen contained several different morphologies in its corresponding SEM fractographs. Inside the reacted zone, different concentrations of Ca, O, and P elements were observed in the two different areas: MCPM for the upper reacted area, and DCPD for the lower reacted area. If the liquid could infiltrate deeper enough, a layer structure of HA

was proposed. Based on the above findings, a functional graded calcium orthophosphate material was obtained in the liquid with a very low concentration of H_3PO_4 .

Except for the above SEM micrographs, some whiskers were frequently found at the interface between the reacted and unreacted zones in the $\text{Ca}(\text{OH})_2/0.06\text{MH}_3\text{PO}_4$ system. CaCO_3 was also being observed if the $\text{Ca}(\text{OH})_2$ green powder compact had been exposed in the air for a period of time. This CaCO_3 phase was not transformed into any orthophosphates during a liquid infiltration at higher pHs. Overall, through a liquid infiltration in this study, different bulk calcium orthophosphate biomaterials were easy to synthesize at room temperature without any further sintering.

Acknowledgements

The authors would like to thank for High Value Instrument Center at I-Shou University for assisting to analyze X-ray diffraction patterns, SEM micrographs, and energy dispersive X-ray spectra (EDXS).

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