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The Alkoxide Sol–Gel Process in the Calcium Phosphate System and its Applications†

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A single calcium glycolate was synthesized. The alkoxide was stable under ambient atmosphere. The calcium glycolate, phosphoric acid and $P(OH)_x(OEt)_{3-x}$ were used as the precursors. Acetic acid was used as a reagent to modify the calcium glycolate and to change the acidity of the mixtures of the precursors. Mixtures of the calcium glycolate and phosphoric acid in a Ca/P ratio of 1.67 showed unusual sol–gel behavior. A transparent gel could be formed depending on the content of acetic acid and the extent of stirring. The behavior is attributed to a high viscosity and a large molecular size of the ethylene glycol solvent, leading to a strong dependence of the reactions in the mixtures on the diffusion process, greatly affected by stirring. When the mixtures of the calcium glycolate and $PO(OH)_x(OEt)_{3-x}$ contained acetic acid at an acetic acid/Ca ratio of 3, stable alkoxide solutions with Ca/P ratios of 1.0, 1.5 and 1.67 could be formed. Different calcium phosphate compounds and hydroxyapatite coatings on alumina substrates could easily be formed from the alkoxide solutions. The chemical homogeneity provided by the alkoxide route leads to easy formation of the required products. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: alkoxide; modification; sol–gel; transparent gel; calcium phosphate; coating

1 INTRODUCTION

The primary step in sol–gel processing is to make an initial solution or sol which is thus capable of providing a homogeneous product.[1,2] The product has a great potential to form a finally required material at a low temperature in the form of bulk material, film, fiber or powder.[2] The hydrolysis of precursors and the condensation of the hydrolyzed species make the main contributions to the sol–gel transition.[3] Only appropriate precursors and solvents can produce the transition. Alkoxides and alcohols are usually used as good precursors and solvents respectively because the hydrolysis of alkoxides is easily controlled by adding a required amount of water and the by-products of the hydrolysis are alcohols.[3] However, some alkoxides have low solubilities in alcohols or high rates of hydrolysis and condensation; these lead to the difficulties in obtaining a homogeneous or transparent gel in a multicomponent system. Chemical modifications to these alkoxides are usually employed to solve these problems. The alkoxyl groups in the alkoxides are exchanged by bigger alkoxyl groups or other more strongly combined ligands such as acetate, acetylacetonate and amines.[4] After modification, the alkoxides are able to form a transparent gel in a single-component system such as copper ethoxide[5,6] and in a multicomponent system.[7] Many alkoxide-derived materials related to silicate, titanate and aluminate systems are successfully prepared because the sol–gel processes of these alkoxides have been thoroughly studied.[8] It is well known that calcium phosphates are also important materials and they are widely used in chemical and biological engineering.[9] Unfortunately, the sol–gel-derived materials in calcium phosphate systems are rarely reported. The difficulties could result from the high rates of hydrolysis and condensation for common calcium alkoxides[10] and from chemical inertia for phosphorus alkoxides.[11] Recently, Livage's work showed that a modified phosphorus alkoxide, $PO(OH)_x(OR)_{3-x}$

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obtained by refluxing an alcoholic solution of P_2O_5, could give a certain chemical reactivity and it could form a transparent gel in a TiO_2–P_2O_5 system.[11] Laine found that calcium glycolate species existed in a bimetallic alkoxide–calcium tri(glycolato)silicate, which serves as a good precursor to silicate glass and ceramic powders.[12] Layroll found that the as-prepared mixture of calcium ethoxide and phosphoric acid produced gelatinous calcium phosphate precipitates.[13] These results provide a basis to gain an insight into the sol–gel process in calcium phosphate systems.

In order to understand the sol–gel process in calcium phosphate systems, it is important for the system to form a transparent gel, because such formation implies that the chemical reactions in the system are well controlled.

The synthesis of the different calcium phosphate compounds by an alkoxide solution route is interesting because the route could provide a simple way to obtain calcium phosphates, as compared with many other wet methods.[14] In addition, hydroxyapatite-coated implants have both good bioactivity and mechanical strength,[15] which is significant in surgery applications. Moreover, the sol–gel route has the possibility of giving an alternative route by which to prepare good hydroxyapatite coatings in view of the fact that the common route, i.e. the spraying method, brings about hydroxyapatite coatings with other unnecessary phases which may not be favorable to the human body.[16]

In this work, a single calcium alkoxide was synthesized by dissolving calcium metal in ethylene glycol. A transparent calcium phosphate gel, various calcium phosphate compounds and hydroxyapatite coatings were prepared via alkoxides; their formation processes are characterized and discussed.

2 EXPERIMENTAL PROCEDURE

2.1 Sample preparation

The calcium glycolate was synthesized by dissolving granular calcium (Merck, Lab) in ethylene glycol (HOGOH) (Prona Lab@ GR), which had been dried by distilling before use. Reflux was performed until the complete dissolution of the granular calcium.

The $PO(OH)_x(OEt)_{3-x}$ solution was formed by dissolving P_2O_5 (Riedel–deHaen) in absolute ethanol (Merck GR) and refluxing for 24 h.[11]

For the synthesis of a transparent gel, phosphoric acid, H_3PO_4 (BOH, Lab, 90%), was used as the phosphorus precursor. Acetic acid (HOAc) (Merck, GR) was added to 0.5 M calcium glycolate solution in HOAc/Ca ratios of 2, 4 and 6 respectively; the mixtures were stirred for 10 min, then, H_3PO_4 at a Ca/P ratio of 1.67 was dropped continually into the calcium glycolate solutions with or without HOAc. During the addition of H_3PO_4, the mixtures were stirred. After completion of the addition, the as-prepared mixtures were sealed by PVA films. Some of the as-prepared mixtures were further stirred for 8 h. After a mixture gelled or precipitated, the gel or precipitates were dried at 150 °C in an oven for 24 h. The dried gel was calcined at 500, 750 and 1000 °C respectively, and the precipitates were calcined at 500 °C.

In the synthesis of different calcium phosphate compounds, the $PO(OH)_x(OEt)_{3-x}$ solution (4 M) was used as the phosphorus precursor. HOAc was added to the calcium glycolate solutions in HOAc/Ca ratios of 1, 2 and 3, then, the $PO(OH)_x(OEt)_{3-x}$ solution was added to the calcium glycolate solutions in Ca/P ratios of 1.0, 1.5 and 1.67. The mixtures with the HOAc/Ca ratio of 3 remained stable for the three Ca/P ratios. These stable solutions were poured onto a hot stainless steel plate (*ca* 150 °C) to evaporate the solvent and obtain gel-like powders. The resulting powders were calcined at 1000 °C for 1 h.

In the preparation of hydroxyapatite coatings on alumina substrates (Hoechst Ceram Tec AG), a liquid film was formed by a dipping method using the stable mixed solution of the $PO(OH)_x(OEt)_{3-x}$ and the calcium glycolate at a Ca/P ratio of 1.67 and an HOAc/Ca ratio of 3. The substrates were dipped into the solution and withdrawn at a rate of 4 cm min^{-1}. The dipped liquid film was dried at 150 °C for at least 15 min and the dried film was heated at 500 °C for 10 min for a run. In order to increase the thickness of the coatings, 10 runs were performed. The coatings with 10 runs were heated at 750 °C for 15 min.

The conditions of the main samples in this work are listed in Table 1.

2.2 Characterizations

2.2.1 ^{31}P nuclear magnetic resonance

^{31}P liquid-state nuclear magnetic resonance (NMR) spectra were examined in a Fourier transform NMR spectrometer (Bruker, AMX 300) at 121.5 MHz with pulse widths of 3.3 μs, recycle delays of 1 s and transients of 15 K

Table 1 The conditions of the samples studied in this work[a]

Sample	P precursor	Ca/P ratio	HOAC/Ca	Remark
C1			1	Solution
C2			2	Solution
C3			3	Solution
C4			4	Solution
CP1	H_3PO_4	1.67	0	Sol when as-prepared
CP1-1	H_3PO_4	1.67	0	Precipitates obtained by further stirring of sample CP1 for 8 h
CP1-2	H_3PO_4	1.67	0	Powders obtained by calcining sample CP1-1 at 500 °C
CP2	H_3PO_4	1.67	2	Sol when as-prepared
CP2-1	H_3PO_4	1.67	2	Precipitates obtained by further stirring of sample CP2 for 8 h
CP2-2	H_3PO_4	1.67	2	Powder obtained by calcining sample CP2-1 at 500 °C
CP3	H_3PO_4	1.67	4	Sol when as-prepared
CP3-1	H_3PO_4	1.67	4	Precipitates obtained by further stirring of sample CP3 for 8 h
CP3-2	H_3PO_4	1.67	4	Powder obtained by calcining sample CP3-1 at 500 °C
CP4	H_3PO_4	1.67	6	Sol when as-prepared
CP4-1	H_3PO_4	1.67	6	Precipitates obtained by further stirring of sample CP4 for 8 h
CP4-2	H_3PO_4	1.67	6	Clear solution after no further stirring, and keeping for one day
CP4-3	H_3PO_4	1.67	6	Transparent gel after keeping sample CP4-2 for about 20 h
CP4-4	H_3PO_4	1.67	6	Cloudy gel after keeping sample CP4-3 for one month
CP4-5	H_3PO_4	1.67	6	Precipitates after keeping sample CP4-4 for one month
CP4-6	H_3PO_4	1.67	6	Powder obtained by calcining sample CP4-1 at 500 °C
CP5	$PO(OH)_x(OEt)_{3-x}$	1.00	0	Heavy precipitation
CP6	$PO(OH)_x(OEt)_{3-x}$	1.00	1	Slight precipitation
CP7	$PO(OH)_x(OEt)_{3-x}$	1.00	2	Very slight precipitation
CP8	$PO(OH)_x(OEt)_{3-x}$	1.00	3	Solution
CP9	$PO(OH)_x(OEt)_{3-x}$	1.50	0	Heavy precipitation
CP10	$PO(OH)_x(OEt)_{3-x}$	1.50	1	Slight precipitation
CP11	$PO(OH)_x(OEt)_{3-x}$	1.50	2	Very slight precipitation
CP12	$PO(OH)_x(OEt)_{3-x}$	1.50	3	Solution
CP13	$PO(OH)_x(OEt)_{3-x}$	1.67	0	Heavy precipitation
CP14	$PO(OH)_x(OEt)_{3-x}$	1.67	1	Slight precipitation
CP15	$PO(OH)_x(OEt)_{3-x}$	1.67	2	Very slight precipitation
CP16	$PO(OH)_x(OEt)_{3-x}$	1.67	3	Solution

[a] The calcium precursor is calcium glycolate.

^{31}P solid-state NMR spectra were measured in a Fourier transform NMR spectrometer (Bruker MSL 400P) at 161.978 MHz with magic-angle spinning and recycle delays of 60 s, and the chemical shifts are quoted in ppm from H_3PO_4 (aq. 85 wt%).

2.2.2 Infrared spectroscopy

Infrared (IR) spectra of the Ca glycolate solutions with different amounts of HOAc were measured in a Fourier transform infrared spectrometer (Mattson Glaxy 7020) with resolution of 4 cm^{-1}. A dismountable liquid cell with KBr windows was used.

2.2.3 X-ray diffraction

X-ray diffraction (XRD) patterns were recorded in an X-ray diffractometer (Rigaku, D/MAX-B) with a step size of 0.05° and a scan speed of 2.00° min^{-1}.

2.2.4 Test of adhesive strength of the coatings

To test the adhesive strength of the coatings, one side with a hydroxyapatite (HAP) layer in a coated sample was removed by polishing with a grinding paper and was carefully cleaned with acetone. Two metallic cylinders of 8 mm in diameter were attached, one to the side with an HAP layer and one to the opposite side without an HAP layer, by a superglue (Permatex® Industrial), respectively. After the glue had polymerized at ambient temperature for 24 h, the adhesive strength of the HAP layer to the substrate was measured by applying a tensile stress to their interface in a

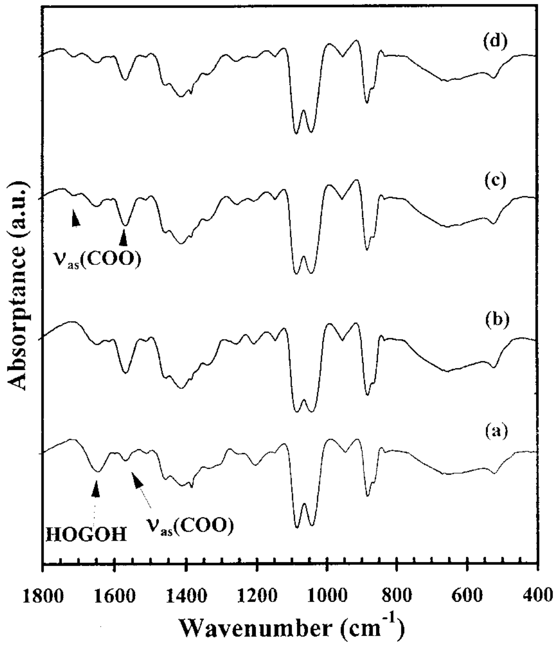

Figure 1 IR spectra of the calcium glycolate solutions with different HOAc/Ca ratios: (a) sample C1 (HOAc/Ca = 1); (b) sample C2 (HOAc/Ca = 2); (c) sample C3 (HOAc/Ca = 3); (d) sample C4 (HOAc/Ca = 4).

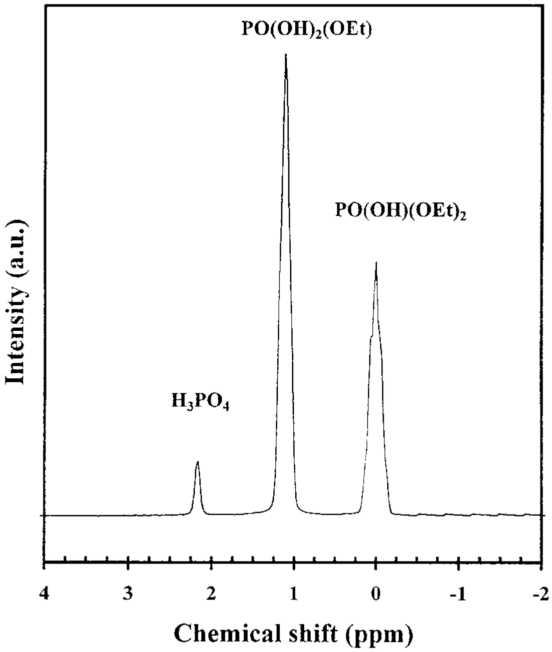

Figure 2 ^{31}P Liquid-state NMR spectrum of the ethanol solution of P_2O_5.

machine (Shimadzu Universal Test Machine, Autograph AG-25TA) with a crosshead speed of 1 mm min^{-1}. At least three measurements were done.

3 RESULTS AND DISCUSSION

3.1 Reactions between the precursors

After the complete dissolution of the granular calcium in the distilled ethylene glycol along with the complete release of bubbles originating from the surfaces of the calcium metal particles, the resulting 0.5 M solution was stable at ambient temperature. Since the bubbles appeared during the dissolution of the calcium metal, it is reasonably considered that a calcium glycolate is formed according to Eqn [1] and the product could be expressed as $Ca(OGOH)_2(HOGOH)_2$ because Ca^{2+} ions need a coordination number of 4 in solution.[17]

$$Ca + HOGOH \rightarrow Ca(OGOH)_2(HOGOH)_2 + H_2\uparrow \quad [1]$$

Its large alkoxy ligands cause calcium glycolate solution to have a lower property to hydrolysis and to be more stable at ambient temperature than common calcium alkoxides.

When HOAc was added to the calcium glycolate solution, samples C1 and 2 showed that the calcium glycolate species were modified, based on the appearance of the ν_{as}(COO) band at 1567 cm^{-1} in their IR spectra, because this band is related to acetate ligands coordinated with Ca species[18] [Fig. 1 curves (a) and (b)]. The reaction between calcium glycolate and HOAc can be written as Eqn [2]. If the HOAc/Ca ratio was more than 2, excess HOAc appeared in the form of free HOAc molecules, because samples C3 and 4 had the ν_{as} (COO) band at 1710 cm^{-1} as well as the ν_{as} (COO) band at 1567 cm^{-1} [Fig. 1(c) and (d)].[18]

$$Ca(OGOH)_2(HOGOH)_2 + HOAC \rightarrow Ca(OAC)_2(HOGOH)_2 \quad [2]$$

The^{31}P liquid-state NMR spectrum (Fig. 2) of the

$$\mathrm{Ca(OGOH)_2(HOGOH)_2 + H_3PO_4 \rightarrow Ca(OGOH)(H_2PO_4)(HOGOH)_2} \quad [3]$$

$$\mathrm{Ca(OGOH)(H_2PO_4)(HOGOH)_2 + H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \cdot \mathit{x}HOGOH \downarrow} \quad [4]$$

$$\mathrm{Ca(H_2PO_4)_2 \cdot \mathit{x}HOGOH + Ca(OGOH)_2(HOGOH)_2 \rightarrow \mathit{m}Ca_3(PO_4)_2 \cdot \mathit{x}HOGOH \downarrow + \mathit{n}CaHPO_4 \cdot \mathit{x}HOGOH \downarrow} \quad [5]$$

solution of P_2O_5 shows that it contains three kinds of P species, mainly $PO(OH)_2(OEt)$ species at 1.13 ppm and $PO(OH)(OEt)_2$ species at 0.02 ppm, and minor H_3PO_4 species at 2.19 ppm.[11]

3.1.1 Reactions between calcium glycolate and H_3PO_4

When H_3PO_4 was added to the Ca glycolate solutions with different HOAc/Ca ratios, the as-prepared mixtures, samples CP1, 2, 3 and 4, had fine precipitates. By further stirring the mixtures for 8 h, the particles in the mixtures grew so large as to be sedimented; the precipitates from the corresponding mixtures are denoted as samples CP1-1, 2-1, 3-1 and 4-1, respectively. If stirring was stopped just after the formation of the as-prepared mixtures, samples CP1, 2 and 3 could stay unchanged for a long time, but sample CP4 became a clear solution after keeping for one day. The resulting solution, sample CP4-2, was transformed to a transparent gel after the solution had been kept for 20 h. A cloudy gel was formed after the transparent gel (sample CP4-3) aged for one month, and finally precipitates (sample CP4-5) appeared after the cloudy gel (sample CP4-4) had aged for one month.

In the mixtures, H_3PO_4 has an ability to react with calcium species, and the presence of H_2O from the H_3PO_4 reagent in an H_2O/H_3PO_4 ratio of about 0.6 can enhance the reactions between H_3PO_4 and calcium species.[19] It is reasonably considered that the Ca glycolate reacts with pure H_3PO_4 droplets during the addition of H_3PO_4; calcium phosphate precipitates are thus easily formed, and cause all the as-prepared mixtures to contain many small precipitated particles. These initial precipitates will further react with the rest of the mixture to form the equilibrated products.

If it is supposed that the reaction of the initial precipitates with the rest in the mixtures proceeds under stirring for 8 h to attain an equilibrium, HOAc shows an influence on the equilibrated precipitates (samples 1-1, 2-1, 3-1 and 4-1) because the XRD patterns (Fig. 3) indicate these precipitates with different CaO/P_2O_5 ratios. The ratios of the maximum peak intensity of β-tricalcium phosphate (β-TCP) to β-$Ca_2P_2O_7$ ($I_{\mathrm{MAX}(\beta\text{-TCP})}/I_{\mathrm{MAX}(\beta\text{-Ca}_2\text{P}_2\text{O}_7)}$) are 2.24, 0.83, 0.23 and 0.00 for samples CP1-2, 2-2, 3-2 and 4-6, respectively. The effects of HOAc on the reactions between the precursors could be explained as follows. For the mixture without HOAc, sample CP1, there are only the calcium glycolate species remaining. The reaction process could be suggested as Eqns [3]–[5].

Equations [3] and [4] lead to the formation of the initial precipitates, and Eqn [5] brings about the formation of the equilibrated precipitates. Since the calcium glycolate species demonstrates a strong basicity [13] and promotes the dissociation of H_3PO_4, sample CP1-1 obtained from Eqn [5] has a large value of *m/n*, i.e. a large CaO/P_2O_5 ratio.

When H_3PO_4 is added to the calcium glycolate solution modified by HOAc in a HOAc/Ca ratio of 2 (sample CP2), the reactant in the remainder of the mixture is mainly $Ca(OAC)_2(HOGOH)_2$ species. The reactions could be suggested as Eqns [6]–[8].

Equations [6] and [7] are considered to form the initial precipitates due to the easy replacement of acetate ligands by phosphate groups in an H_3PO_4-rich system and Eqn [8] leads to the formation of the equilibrated precipitates. Since the basicity of $Ca(OAc)_2(HOGOH)_2$ is less than that of $Ca(OGOH)_2(HOGOH)_2$,[20] sample CP2-1 obtained from Eqn [8] will have a lower *m/n* ratio.

When H_3PO_4 is added to the calcium glycolate solutions modified by HOAc in an HOAc/Ca ratio

$$\mathrm{Ca(OAC)_2(HOGOH)_2 + H_3PO_4 \rightarrow Ca(OAC)(H_2PO_4)(HOGOH)_2} \quad [6]$$

$$\mathrm{Ca(OAC)(H_2PO_4)(HOGOH)_2 + H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \cdot \mathit{x}HOGOH \downarrow} \quad [7]$$

$$\mathrm{Ca(H_2PO_4)_2 \cdot \mathit{x}HOGOH \cdot + Ca(OAc)_2(HOGOH)_2 \rightarrow \mathit{m}Ca_3(PO_4)_2 \cdot \mathit{x}HOGOH \downarrow + \mathit{n}CaHPO_4 \cdot \mathit{x}HOGOH \downarrow} \quad [8]$$

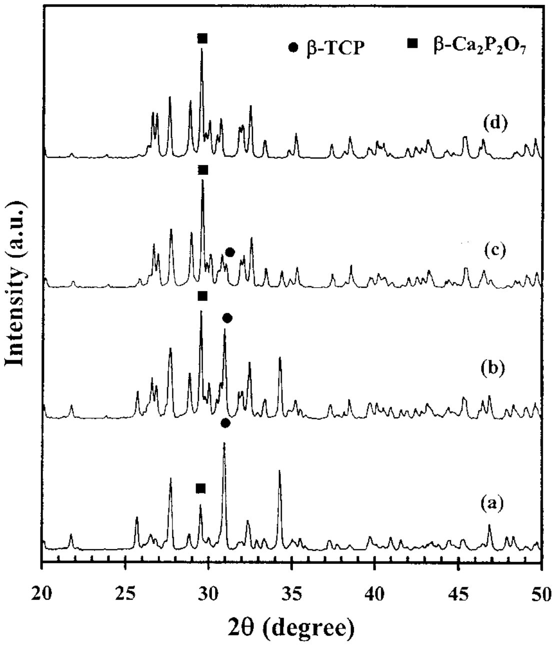

Figure 3 XRD patterns of: (a) sample CP1-2 (HOAc/Ca = 0); (b) sample CP2-2 (HOAc/Ca = 2); (c) sample CP3-2 (HOAc/Ca = 4); (d) sample CP4-6 (HOAc/Ca = 6).

of more than 2 (samples CP3, and 4), the remainder of the mixture contains mainly the reactants, $Ca(OAc)_2(HOGOH)_2$ species and free HOAc molecules. The reactions of the formation of the initial precipitates can be considered as the same as Eqns [6] and [7]; the reactions of the initial precipitates with the remainder of the mixtures to form the equilibrated precipitates could be written as Eqns [9] and [10].

Equation [9] leads to the dissolution of the initial precipitates because the free HOAc can play roles in stabilizing the combination of acetate ligands with calcium ions and increasing the acidity of the mixture. If the mixture is stirred for a long time, a homogeneous environment is provided and Eqn [10] can be greatly accelerated. The newly and quickly formed particles act as nuclei to induce the formation of more equilibrated particles. The HOAc still plays a role in lowering the *m/n* ratio in the precipitates obtained from Eqn [10] compared with those from Eqn [8]. Hence, the corresponding $I_{\mathrm{MAX}(\beta\text{-TCP})}/I_{\mathrm{MAX}(\beta\text{-Ca}_2\text{P}_2\text{O}_7)}$ ratios decrease to 0.23 and 0.00 for samples CP3-2 and 4-6 [Fig. 3, curves (c) and (d)], respectively. The lack of appearance of β-TCP in sample CP4-6 implies that the equilibrated precipitates, sample CP4-1, could be in the form of $CaHPO_4{\cdot}x$HOGOH, which conforms with the case in an aqueous system with a low pH value.[17]

3.1.2. Reactions between calcium glycolate and $PO(OH)_x(OEt)_{3-x}$

In this work, the $PO(OH)_x(OEt)_{3-x}$ solution contained a large amount of $PO(OH)_2(OEt)$, a medium amount of $PO(OH)(OEt)_2$, and a small amount of H_3PO_4, as shown in Fig. 2. When the calcium glycolate solutions were mixed with the $PO(OH)_x(OEt)_{3-x}$ solution in different Ca/P ratios, precipitates appeared immediately in samples CP5, 9 and 13. The addition of HOAc to the mixtures could minimize and eliminate the precipitation, depending on the amounts of HOAc added, as shown in Table 1. If the HOAc/Ca ratio was 3, samples CP8, 12 and 16 could become stable solutions.

H_3PO_4, $PO(OH)_2(OR)$ and $PO(OH)(OR)_2$ are usually considered as very reactive, moderately reactive and almost inert, respectively.[11] When the calcium glycolate solution is mixed with the $PO(OH)_x(OEt)_{3-x}$ solution, the calcium species mainly react with H_3PO_4 species as mentioned above, leading to immediate precipitation. Hence, H_3PO_4 could be considered as a main contributor to the precipitates.

When the $PO(OH)_x(OEt)_{3-x}$ solution was added to the calcium glycolate solutions with HOAc, the modified calcium glycolate species would not react so strongly with the H_3PO_4 species. If free HOAc exits, the mixtures can remain as stable solutions because the $PO(OH)_x(OEt)_{3-x}$ solution contains a small amount of H_3PO_4 species and free HOAc depresses the reactions between the modified calcium glycolate and H_3PO_4 by increasing the acidity.

3.2 Formation of a transparent gel

The reaction (Eqn [10]) of the initial precipitates to

$$\mathrm{Ca(H_2PO_4)_2}\cdot x\mathrm{HOGOH} + \mathrm{HOAc} \rightarrow \mathrm{Ca(OAc)(H_2PO_4)(HOGOH)_2} \qquad [9]$$

$$\begin{aligned}\mathrm{Ca(OAc)(H_2PO_4)(HOGOH)_2} + \mathrm{Ca(OAc)_2(HOGOH)_2} \rightarrow\ & m\mathrm{Ca_3(PO_4)_2}\cdot x\mathrm{HOGOH}\downarrow + \\ & n\mathrm{CaHPO_4}\cdot x\mathrm{HOGOH}\downarrow \end{aligned} \qquad [10]$$

form the equilibrated product involves the removal of the solvated HOGOH molecules and the diffusion of the species. These processes could be retarded by the large molecular size and high viscosity of the ethylene glycol solvent. The reaction will proceed sluggishly when stirring is stopped just after the completion of the addition of H_3PO_4. If the remainder of the mixture has a high acidity, the initial precipitates can be completely dissolved according to Eqn [9] and the soluble calcium phosphate species can be kept for a long time due to the absence of induction of solid particles. Hence, only the mixture with the highest HOAc/Ca ratio, sample CP4, is able to form a clear solution, and the solution may contain $Ca(OAc)(H_2PO_4)(HOGOH)_2$ and $Ca(OAc)_2(HOGOH)_2$ species. When the solution ages, the species in the solution have a thermodynamic tendency to associate with each other to form an equilibrated product which appears as precipitates like sample 4-1. Since this association tendency is exerted homogeneously on each species in the solution, gelation can occur instead of precipitation. According to the NMR spectrum of the transparent gel [Fig. 4, curve (a)], most of the P species are not combined very strongly with the calcium species due to a strong peak at 0.74 ppm and some exist as oligomers of calcium phosphate due to a weak peak at 3.25 ppm. In the gel, the phosphate groups could be considered to bond to the free HOAc molecules by hydrogen bonding because H and O atoms in both have a relatively high static electric force. This leads to a small shift of the phosphate groups in the NMR spectrum of the gel. The formation of the transparent gel network can be suggested to be built from oligomeric calcium phosphate species, monomeric calcium phosphate species and unreacted calcium species through a hydrogen bonding connection (Eqns [11] and [12]).

Equation [11] indicates that the soluble species are associated by hydrogen bonding, and Eqn [12] denotes the crosslinking of the associated calcium phosphate species by unreacted calcium species and calcium phosphate oligomers. When the values of *m, n* and *l* are large enough, a gel can be formed. Because the calcium species contain solvated molecules and the phosphorus species have hydrogen-bonded HOAc molecules in the gel, the gel can appear transparent.[22]

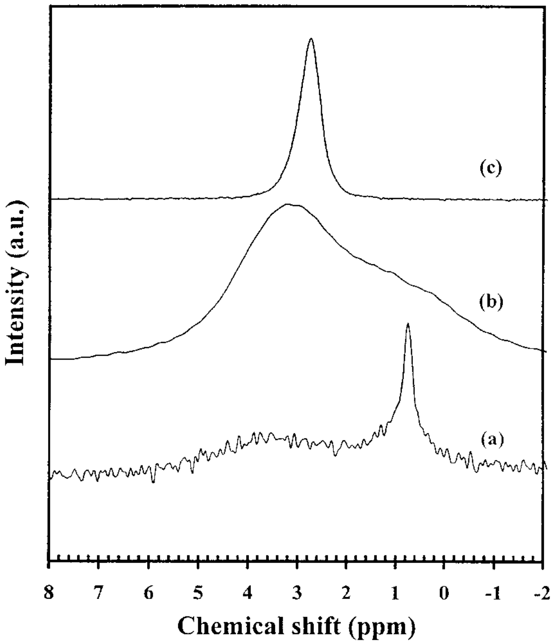

Figure 4 ^{31}P solid-state NMR spectra of sample CP4-3 heated at (a) unheated; (b) 150 °C; (c) 750 °C.

When the transparent gel is heated at 150 °C, a similar structure in the gel to hydroxyapatite can be formed by removing acetate ligands and rearranging the structure as shown in Figs 4, curve (b), and 5, curve (a). This implies that the gel has a good homogeneity. When the gel is further heated at a higher temperature, the hydroxyapatite phase develops better according to a narrower NMR peak at 2.75 ppm [Fig. 4, curve (c)] and stronger XRD intensities in [Fig. 5, curves (b), (c) and (d)].

When the transparent gel ages, the gel structure tries to rearrange itself to a thermodynamically equilibrated one, causing the transparent gel to be couldy, and even to precipitate. The precipitate after calcination at 500 °C becomes a pure β-$Ca_2P_2O_7$ phase, as the same as sample CP4-6 [Fig. 3, curve (d)].

$$n\mathrm{Ca(OAC)(H_2PO_4)(HOGOH)_2} \rightarrow \{\mathrm{Ca(OAc)(H_2PO_4)(HOGOH)_2}\}_n \qquad [11]$$

$$\begin{aligned}&\{\mathrm{Ca(OAc)(H_2PO_4)(HOGOH)_2}\}_n + m\mathrm{Ca(OAc)_2(HOGOH)_2} + l\{\mathrm{Ca(OAc)_3PO_4}\} \rightarrow \\ &\{\mathrm{Ca(OAc)(H_2PO_4)(HOGOH)_2}\}_n \cdot m\mathrm{Ca(OAc)_2(HOGOH)_2} \cdot l\{\mathrm{Ca(OAc)_3PO_4}\} \qquad [12]\end{aligned}$$

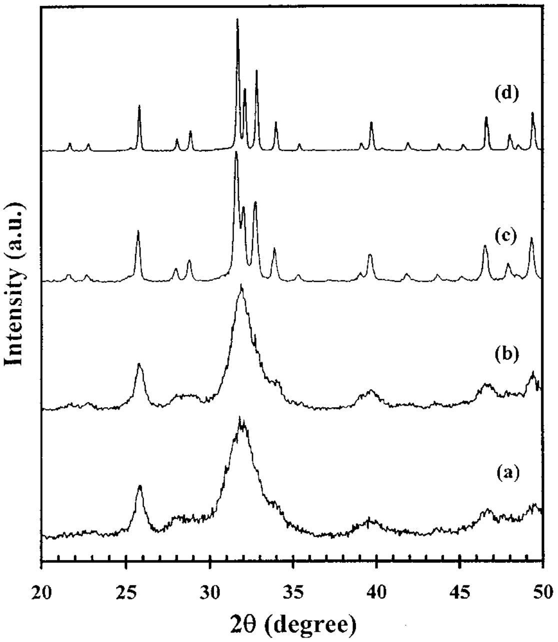

Figure 5 XRD patterns of sample CP4-3 heated at: (a) 150 °C; (b) 500 °C; (c) 750 °C (d) 1000 °C.

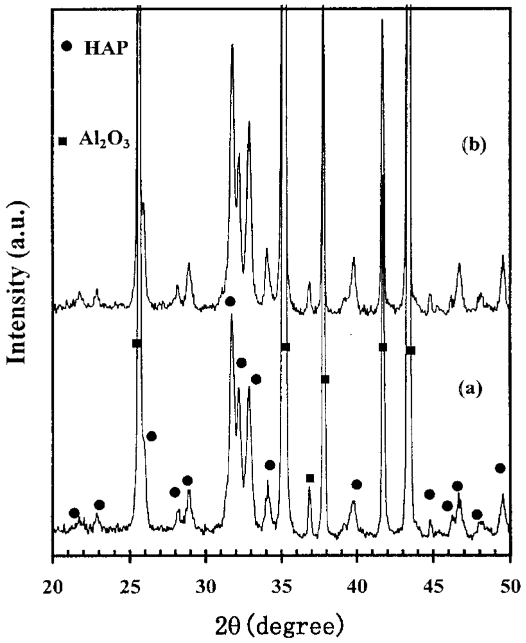

Figure 7 XRD patterns of the coatings obtained at (a) 500 °C; (b) 750 °C.

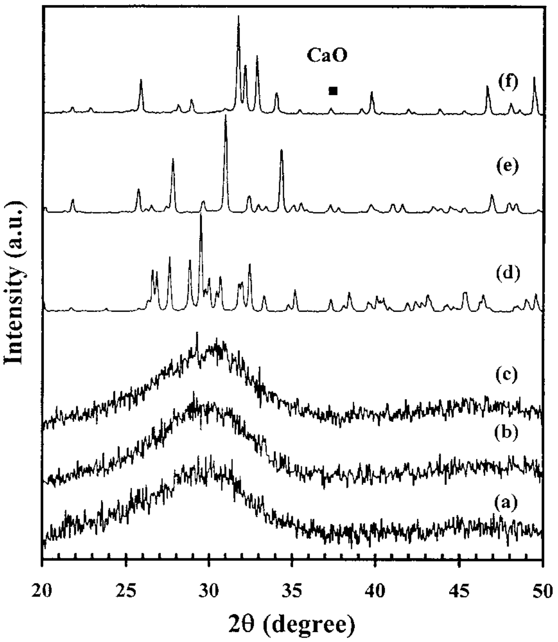

Figure 6 XRD patterns of the gel-like powders without calcination obtained from: (a) sample CP8; (b) sample CP12; (c) sample CP16. XRD patterns of the powders after calcination at 750 °C obtained: (d) from (a); (e) from (b); (f) from (c).

3.3 Synthesis of calcium phosphates

Samples CP8, 12 and 16 were each poured onto a hot plate, respectively, and were transformed to gel-like powders. These gel-like powders were then calcined at 1000 °C.

The XRD patterns of the gel-like powders derived from samples CP8, 12 and 16 show that they are amorphous [Fig. 6, curves (a), (b) and (c)] and the XRD patterns [Fig. 6, curves (d), (e) and (f)] of the calcined powders show that the powder derived from sample CP8 changes to a pure $Ca_2P_2O_7$ phase; the powder derived from CP12 changes to a β-TCP phase; and the powder derived from CP16 changes to a hydroxyapatite phase containing a very small amount of CaO.

The easy synthesis of the different calcium phosphate compounds could be attributed to the inclusion of a gelation in the process. When the stable solutions are heated on the hot plate, the solvent evaporates. During concentration of the solutions, the calcium and phosphorus species approach each other, and they enter into a gelation process to become gel-like powders. After gelation, the resulting product could keep the chemical homogeneity which leads to its existence as an

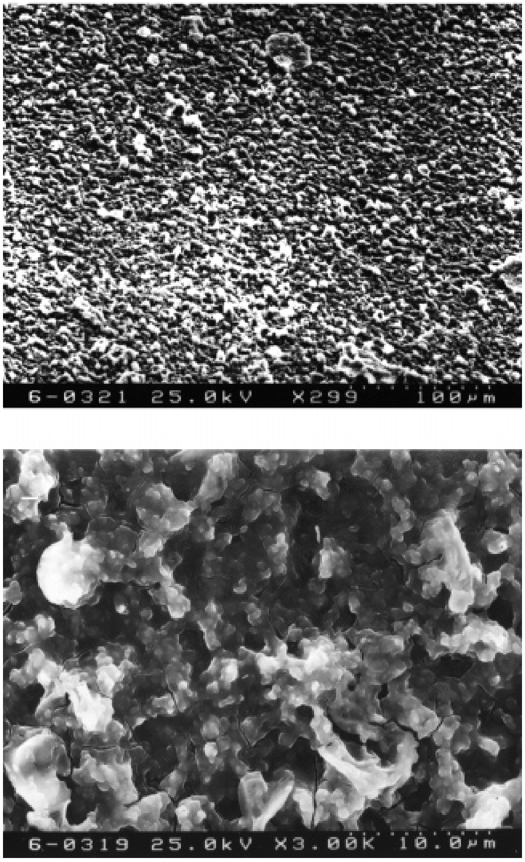

Figure 8 SEM micrographs of the hydroxyapatite coating on alumina substrate obtained at 750 °C.

amorphous state, and to the formation of a calcium phosphate phase as designed in the initial solution after calcination.

3.4 Hydroxyapatite coatings

When sample CP16 was used as a dipping solution, pure hydroxyapatite phase coatings on alumina substrates were formed (Fig. 7), and the coatings had a porous or rough surface (Fig. 8) which is favorable for the growth of bone tissues.[21] With an increase in heating temperatures the HAP crystalline phase in the coatings was better developed. The intensities of the peaks in the coating heated at 750 °C were about twice as high as that of the peaks in the coating prepared at 500 °C (Fig. 7).

The adhesion strength for the coating heated at 1000 °C was 10.0 ± 2.8 MPa. This value shows that the bonding between the alumina substrate and the coating is strong and could include a contribution by a chemically combination, although their XRD patterns do not show any extra phases formed.

4 CONCLUSION

Since calcium glycolate has large alkoxy ligands, its solution is more stable at ambient temperature than other common Ca alkoxides.

Acetic acid plays important roles in obtaining a transparent gel and stable solutions in the calcium glycolate–H_3PO_4· and the calcium glycolate–$PO(OH)_x(OEt)_{3-x}$ systems because HOAc can modify the Ca glycolate species, increase the acidity in the mixtures and retard the reactions between Ca glycolate and either H_3PO_4 or $PO(OH)_x(OEt)_{3-x}$.

A transparent gel can be formed from the mixture of the calcium glycolate and H_3PO_4 in a Ca/P ratio of 1.67 when the mixture contains an HOAc/Ca ratio of 6 and is not further stirred just after the addition of H_3PO_4.

Different calcium phosphate compounds can be formed easily from the solutions of the calcium glycolate and $PO(OH)_x(OEt)_{3-x}$ with an HOAc/Ca ratio of 3 and corresponding Ca/P ratios.

From a stable solution obtained from the calcium glycolate and $PO(OH)_x(OEt)_{3-x}$ with a HAOC/Ca ratio of 3 and a Ca/P ratio of 1.67, hydroxyapatite coatings on alumina substrates can be prepared by a dipping method. The resulting coating shows a pure hydroxyapatite phase and a good adhesive strength of 10 ± 2.8 MPa.

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REFERENCES

1. D. Segal, *Chemical Synthesis of Advanced Ceramic Materials, Chemistry of Solid State Materials*, vol. 1. Cambridge University Press, Cambridge, 1989, pp.33–88.
2. J. Brinker and G. W. Scherer, *Sol–Gel Science: the Physics and Chemistry of Sol–Gel Processing*, Academic Press, New York, 1992, pp.21–96, 839–870.
3. L. L. Hench and J. K. West, *Chem. Rev.* **90**, 33 (1990).
4. J. Livage, M. Henry and C. Sanchez, *Prog. Solid State Chem.* **18**, 259 (1988).

5. W. Weng, Z. Ding and F. Zhang, *J. Non-Cryst. Solids* **147–148**, 102 (1992).
6. W. Weng, J. Yang and Z. Ding, *J. Non-Cryst. Solids* **170**, 134 (1994).
7. J. Yang, W. Weng and Z. Ding, *J. Sol–Gel Sci. Technol.* **4**, 187 (1995).
8. R. C. Mehrotra, Present status and future potential of the sol–gel process. In: *Chemistry, Spectroscopy and Applications of Sol–Gel glasses*. Reisfeld, R. and Jorgensen, C. K. (eds), *Structure and Bonding* vol. 77, Springer-Verlag, Berlin, 1992, pp.1–36.
9. B. Narasaraju and D. E. Phebe, *J. Mater. Sci.* **31**, 1 (1996).
10. J. Li, Bachelor's Thesis, Zhejiang University, 1992.
11. J. Livage, P. Barboux, M. T. Vandenborre, C. Schmutz and F. Taulelle, *J. Non-Cryst. Solids* **147–148**, 18 (1992).
12. P. Kansal and R. M. Laine, *J. Am. Ceram. Soc.* **78**, 529 (1995).
13. P. Layrolle and A. Lebugle, *Chem. Mater.* **8**, 134 (1996).
14. Y. Suwa, H. Banno, M. Mizuno and H. Saito, *J. Ceram. Soc. Jpn., Int. Ed.* **101**, 642 (1993).
15. M. Shirkhanzadeh, *J. Mater. Sci.: Mater. Med.* **6**, 90 (1995).
16. T. Brendel, A. Engel and C. Russel, *J. Mater. Sci.: Mater. Med.* **3**, 175 (1992).
17. W. Mooney and M. A. Aia, *Chem. Rev.* **61**, 434 (1961).
18. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd edn, Wiley–Interscience, New York, 1979, p. 220.
19. D. Corbridge, *Phosphorus: an Outline of its Chemistry, Biochemistry and Technology*, 3rd edn, *Studies in Inorganic Chemistry*, vol. 6, Elsevier, Amsterdam, 1985, pp.120–208
20. M. Henry, J. P. Jolivet and J. Livage, Aqueous chemistry of metal cations: hydrolysis, condensation and complexation. In: *Chemistry, Spectroscopy and Applications of Sol–Gel Glasses*, Reisfeld, R. and Jorgensen, C. K. (eds), *Structure and Bonding* vol. 77, Springer-Verlag, Berlin, 1992, pp.153–206
21. S. Hirano, T. Yogo, K. Kikuta, K. Noda, M. Ichida and A. Nakamura, *J. Am. Ceram. Soc.* **78**, 2956 (1995).
22. W. Weng, J. Yang and Z. Ding, *J. Non-Cryst. Solids* **169**, 177 (1994).