Sol–gel prepared β-TCP/FHA biphasic coatings

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Abstract

β-tricalcium phosphate/fluoridated hydroxyapatite (β-TCP/FHA) biphasic coatings were prepared on titanium alloy substrate by means of sol–gel method. The coatings combine the initial dissolution of β-TCP with the long-term stability of FHA to create a high quality bioactive coating. Ca(NO3)2, P2O5 and HPF6 were dissolved in ethanol respectively and mixed in designed sequence and Ca:P:F ratios to form a sol. After the sol was refluxed for 24 h, the as-refluxed sol was used for FHA coating. β-TCP powders were dispersed into the sols to form colloidal sols for β-TCP/FHA biphasic coatings. The as-refluxed sols with different Ca:P:F ratios only resulted in apatite coatings with low F content. Biphasic coatings were prepared with the colloidal sols. The β-TCP contents of the coatings could be tailored by varying the amount of the powders in the colloidal sols. The surface morphology of the coatings becomes rougher with increasing amount of the powders, which favors cell attachment. However, excessive amount of powders results in powder agglomeration, leading to more cracks in the coatings. Fine powders and good dispersion are essential factors for good biphasic coatings.

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1. Introduction

Hydroxyapatite (HA) coatings have been widely investigated for application on surface of biomedical metals to improve bonding and interaction between body tissue and implant [1]. One of the major concerns of such coatings is its large solubility in body fluid that results in instability after long-term implantation [2,3]. One approach is to incorporate fluorine into the HA structure to form fluoridated hydroxyapatite (FHA) [4–6] to render the coatings more dissolution resistance.

FHA coatings have been studied extensively in recent years. Aside from the reduction in solubility, the incorporation of F is found to possess other effects: certain F concentration is beneficial to implant–cell interactions and cell attachment [7–9], but high dose of F adversely affects cell activity [9]. The reason could be attributed to that the initial dissolution of the coatings leads to higher concentration of Ca2+ or PO43− at the vicinity of the implant thus helps the cell activities and osteointegration [10–12], since both Ca2+ and PO43− ions are crucial to many biochemical reactions [13]. However, for long-term stability, the coating should be dissolution resistant as far as possible. Hence, a good coating should have both properties: short term dissolution and long term dissolution-resistance. A biphasic coating that has two distinct Ca phosphate phases, a soluble phase and a dissolution-resistant matrix, is suggested to be capable of possessing the above properties.

It has been reported that plasma sprayed HA/β-TCP biphasic coatings showed good early implant tissue interaction due to the existence of β-TCP [14], however, since the matrix is still HA, the long term effect may still be a concern.

Therefore, FHA phase seems ideal to be dissolution-resistant matrix because of its small solubility and comparable good biocompatibility over HA. Also, FHA coating has been reported to form dense and strong interface when applied on Ti6Al4V substrate [15], which reduce the risk of debris detachment and further ensure the long-term stability of coatings. As for the soluble phase, β-TCP phase could be a good candidate: many studies have proved it has good biocompatibility [16–18] and biodegradability, its solubility is much larger that of pure HA: pKsp, β-TCP = 29.5, pKsp, HA = 117.2 [19].

In this paper, FHA is chosen as the dissolution-resistant matrix and the β-TCP as the soluble phase. The biphasic coatings are prepared by sol–gel method. The relative phase
composition and fluorine content of the coatings are characterized. The morphology, especially the effect of powder addition on morphology is discussed.

2. Experimental

Calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, GR, Merck) was dissolved in ethanol (GR, Merck) to form the 2 mol/L “Ca-precursor”; ethanol was gradually poured into phosphor pentoxide (P₂O₅, GR, Merck) to form 2 mol/L solution which was refluxed for 24 h to become the “P-precursor”. Designed amount of HPF₆ was added drop-wise into the P precursor. After that, the Ca precursor was added into the mixture in designed Ca/P ratio. Based on many wet chemical calcium phosphate synthesis researches [20], β-TCP can be easily formed when the Ca/P ratios are smaller than the stoichiometric value of HA (1.67). Thus, the Ca/P ratios in the mixture were designed to be 1.30, 1.40, 1.50 and 1.67, respectively. These mixed solutions were further refluxed for 24 h to be as-refluxed sols.

Commercial β-TCP powders (Fluka, purum) were also directly added in the refluxed sol with a Ca/P ratio of 1.67 and ultrasonically dispersed for 20 min to be the “colloidal sol”. The amount of powders added is determined through the R value defined as Caₚowders(mol)/Caₚ₀(sol(mol)).

Titanium alloy (Ti–6Al–4V) substrates were polished down to #1200 grade SiC paper. The substrates were rinsed in double distilled water and ultrasonically washed in acetone for ten minutes and dried before coating. The substrates were dipped in the sols and withdrawn at a speed of 8 cm/min. The sol-coated substrates were then immediately transferred to an oven at 150 °C and held for 15 min to dry, and then fired in a furnace at 600 °C for 15 min. For coatings derived from as-refluxed sols with different Ca/P ratios, such coating process was repeated for 5 times to reach a coating thickness of 1~1.5 μm. As for those coatings from colloidal sols, only two dipping runs were done, the bottom layer was prepared with as-refluxed sol having Ca:P:F=5:3:1, which would lead to a bottom FHA layer eventually; the top layers were prepared on them with colloidal sols with different R ratios (0, 1/4, 1/2, 3/4 and 1/1).

The coatings were characterized with X-ray Diffractometry (XRD, RIGAKU, D-Max, RA, 2°/min, 0.02° per step) for phase identification. X-ray Photoelectron Spectroscopy (XPS, AXIS Kratos Ultra, Aluminum mono, 1 eV per step) was used for characterization of fluorine content of the coating. The proportions of crystalline phase of the coatings are evaluated by two means: 1) the areas of the (0 2 10) peak of β-TCP and the (2 1 1) peak of FHA (after deconvolution) are measured and compared in terms of Caₐ-TCP/CaₕHA molar ratios; 2) from the XPS result, the nominal F content of the coatings in term of F/Ca ratios can be written as F/(Caₐ-TCP+CaₕHA), since all the FHA precursor have the same F content (fixed F/CaFHA value of 0.2), the Caₐ-TCP/CaₕHA ratios of all the coatings are obtained. The surface morphology of the coatings was observed through the SEM (JEOL, JSM5600LV). For the thickness of the coatings, the sample was embedded in resin and polished from cross-sectional direction down to #2000 grade SiC paper, then observed at SEM.

3. Results and discussions

3.1. Coatings prepared from as-refluxed sols having different starting Ca/P ratios

As shown in the Fig. 1, all the coatings demonstrate pure apatite phase, even when the Ca/P ratio in the starting sols is down to 1.30. The F contents in terms of F/Ca ratio are plotted in Fig. 2 as a function of Ca/P ratio. As is obvious from Fig. 2, with decreasing Ca/P ratio, the fluorine content of the coating decreases rapidly. At Ca/P ratio of 1.30, there is almost no fluorine.

At low Ca/P ratio, excessive acidic phosphate groups appear in the dipping sol that interfere the formation of FHA during drying and firing; these acidic groups react with the intermediate nanoscale CaF₂ and compete with the formation of FHA [21], leading to the formation and escape of volatile compounds containing F and P. Furthermore, as reported [22,23], calcium deficient apatite could be easily formed when the starting Ca/P ratio is low, only after high temperature firing (over 1000 °C), which is unfavorable to the metallic substrate, β-TCP phase could be formed. Resulted from both factors, the coatings obtained are actually apatite with very low F concentration.
3.2. Coatings prepared from colloidal sols with different R values

The XRD patterns of the coatings prepared with colloidal sols were shown in Fig. 3: with exception of R=1/4, β-TCP phase and apatite phase were clearly observed on all other patterns. The relative β-TCP phase content was evaluated by comparing the areas of the strongest peak of β-TCP and FHA. For R=1/4, 1/2, 3/4 and 4/4, the β-TCP phase content is 0, 14%, 24% and 32%, respectively. This illustrate the β-TCP content in the coating is tailored by varying the amount of powders dispersed in the sols, however, when the R value is low (R=1/4), no β-TCP phase detected because it falls out of the detection limits.

XPS characterization of the coatings revealed that the coatings contain fluorine, the nominal F content in term of F/Ca ratio in the FHA phase, as shown in Fig. 4, decreased with increasing β-TCP content until the F content stopped decreasing. Such results do mean the β-TCP powders are homogeneously distributed in the FHA matrix, including the coating surface. However, there is an abnormal changes of nominal F content for coating with R=1/4, the reason for that will be discussed later.

Considering the two layers of the coating were prepared from as-refluxed sol and colloidal sols, respectively, the coatings actually had a bottom FHA layer that ensured good interface with the substrate [15] and β-TCP/FHA top layers for desired function.

3.2.1. The morphology of the coatings and the effect of powders

Since there are powders dispersed in the dipping sol, the morphology of the resulted coatings is strikingly different from those of the pure FHA coatings: in Fig. 5, the morphology of the pure FHA coating (Fig. 5A) is smooth and dense. After the powders are dispersed in the sols, at R=1/4, the coating shows individual particles in the coatings (Fig. 5B), the size of powders is around 1~5 microns, which is in well accordance with the original β-TCP powders; with even higher powder content, R=1/2, the powders agglomerate into clusters (Fig. 5C), accompanying by cracks around these clusters. At even higher powder content, R=3/4, more cracks are observed (Fig. 5D). Further increased powder amount (R=1/1) leads to even more cracks and then results in the formation and detachment of small debris (Fig. 5E). This result also explains why the coating with R=1/1 has abnormal nominal F content, because of the detachment of debris, the bottom layer which is almost a pure FHA exposed, result in more F signal detected.

From the SEM observation, the existence and increase of β-TCP powders greatly affect the morphology of the coatings: more cracks resulted with increasing powder amount. Two reasons could be responsible:

1. Thickening of the coating by the powders. The wettability between the β-TCP particles and the dipping sols is good, which could be proven by the well dispersion and stability of the dispersed sol. Consequently, a thicker liquid layer would surround a particle on the substrate, resulting in thicker coating around the vicinity of the particle. With increased distance from the particle, the thickness decreased gradually to the normal. However, if the distance between two particles is short enough, thicker coating will be remained between them, as shown schematically in Fig. 6. As a result, with the increased amount of powders (increasing R value), the overall coating thickness is increased. Fig. 7 showed the SEM cross-section images of FHA and β-TCP/FHA coatings: without powders the coating thickness is 1 micron after five dipping (Fig. 7A); with powders, R=3/4, 3~4 micrometers at only 2 dipping runs (Fig. 7B). Thick coatings will result in the accumulation of residual stress, leading to the formation of cracks.

2. Mismatch of the coefficients of thermal expansion (CTE). The CTE of the pure fluorapatite (FA) and HA are about 10×10⁻⁶ °C⁻¹ [24] and 13×10⁻⁶ °C⁻¹ [24,25], respectively. As a solid solution between both, the CTE of FHA could be estimated by linear interpolation between the two values. Therefore, since the F content in the FHA matrix is quite similar to pure FA, its CTE is supposed to be very close to

![Fig. 3. XRD patterns of the coatings from colloidal sols with different R values.](image)

![Fig. 4. F content in term of F/Ca ratios of the β-TCP/FHA coatings from the colloidal sols with different powder loading.](image)
FA’s. However, it is reported β-TCP has an even higher CTE than HA \cite{25}, that indicates the mismatch of thermal expansion between the FHA matrix and β-TCP is not neglectable. Such effects will result in stress at the β-TCP-FHA boundaries, which, initiate cracks from the boundaries, as shown in Fig. 5C and D.

Between the two reasons, the thickness increase of the coatings is regarded as the main reason, because the cracks appear not only around the powders, but also on those areas away from the powders. However, the effect of CTE mismatch could not be excluded because the cracks do exist around the particles or initiate from the β-TCP-FHA boundaries. With the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image1.png}
\caption{Surface morphology of the coatings from the colloidal sols with different powder loading: A, pure FHA; B, $R=1/4$; C, $R=1/2$; D, $R=3/4$; E, $R=1/1$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image2.png}
\caption{Cross-section schematic figure of the coating derived from colloidal sols.}
\end{figure}
increase of the amount of particles in the coatings, more cracks are resulted, leading to the formation and detachment of debris, which could be seen in Fig. 5E. Agglomeration of the particles aggravates this effect since agglomeration creates larger particles. Therefore, smaller particle size and better powder dispersion could be favorable condition for preparation of such coatings.

3.2.2. β-TCP content of the coating

Fig. 8 plots the relative β-TCP in the resultant coatings against that R value in the sol. The point at $R = 1/1$ is excluded from the plot because at $R = 1/1$ there are many debris detachment occurred in the coating. Both XRD and XPS data further proved that the β-TCP content increased with increased R ratio in the dipping sol, however, the value obtained form XPS result is much higher than those obtained from XRD patterns.

Based on the designed coating structure, the bottom layer is actually pure FHA and the top layer is β-TCP/FHA. What XRD patterns give is the overall information of both layers (because of the X-ray penetration). Therefore, the ratio obtained is actually the β-TCP in the top layer to the FHA phase in the whole coatings. Furthermore, due to the sensitivity limit, although there are many particles observed on the coating surface of $R = 1/4$, the correct Ca content is not captured by XRD.

XPS results are uniformly higher than the XRD-based results. At $R = 1/4$, XRD fails to find β-TCP on the surface, but XPS reveals its existence. Obviously, since the XPS only measures the very surface layer of the coatings, the bottom FHA layer will not affect its result. Thus, more accurate surface β-TCP content of the coatings is obtained.

In the real case application or in vitro cell culture, the initial dissolution happens only on the surface layers of the coatings, it is estimated only about several hundred of nanometer thick layer is involved. As such, XPS phase content results could serve as a good guide.

4. Conclusion

In order to optimize the dissolution behavior of calcium phosphate coatings, biphasic coatings are prepared and characterized.

1. Biphasic β-TCP/FHA coatings are obtained by dispersing β-TCP powders in FHA precursor sol. The coatings have a structure of FHA functioning as the matrix in which β-TCP particles are dispersed.
2. The β-TCP content is better characterized by XPS than by XRD due to the nature of the biphasic structure.
3. The coating morphology is greatly affected by the particle size and powder amount: relatively large particles show thickening effect leading to thicker coatings and more cracks; large amount of powders will result in powder agglomeration. Therefore, smaller particles and better dispersion should be emphasized in future work.

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