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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. $Ca(NO_3)_2$, P_2O_5 and HPF_6 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.

Keywords: β-tricalcium phosphate; Fluoridated hydroxyapatite; Biphasic; Coatings

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 Ca^{2+} or PO_4^{3-} at the vicinity of the implant thus helps the cell activities and osteointegration [10–12], since both Ca^{2+} and PO_4^3 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: $pK_{sp,\ \beta\text{-TCP}}=29.5$, $pK_{sp,\ HA}=117.2$ [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

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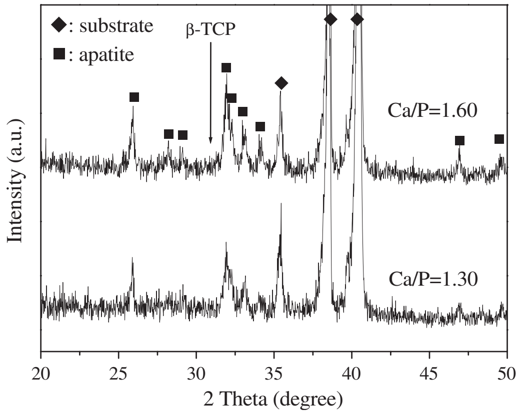

Fig. 1. Typical XRD patterns of coatings from as-refluxed sols with different starting Ca/P ratio.

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 ($Ca(NO_3)_2{\cdot}4H_2O$, GR, Merck) was dissolved in ethanol (GR, Merck) to form the 2 mol/L “Ca-precursor”; ethanol was gradually poured into phosphor pentoxide (P_2O_5, GR, Merck) to form 2 mol/L solution which was refluxed for 24 h to become the “P-precursor”. Designed amount of HPF_6 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 Ca_{powder}(mol)/Ca_{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 $Ca_{\beta\text{-TCP}}/Ca_{FHA}$ molar ratios; 2) from the XPS result, the nominal F content of the coatings in term of F/Ca ratios can be written as $F/(Ca_{\beta\text{-TCP}}+Ca_{FHA})$, since all the FHA precursor have the same F content (fixed F/Ca_{FHA} value of 0.2), the $Ca_{\beta\text{-TCP}}/Ca_{FHA}$ 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 CaF_2 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.

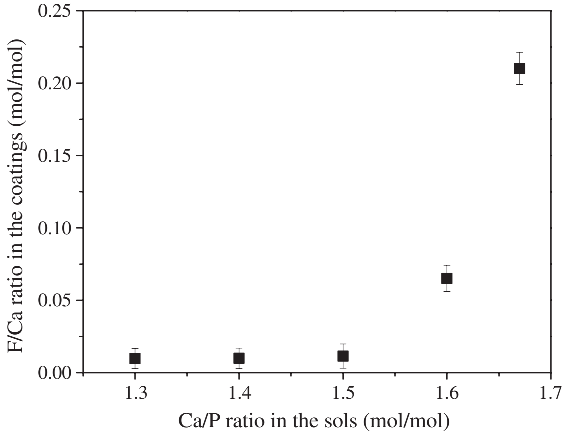

Fig. 2. F content of the coatings from as-refluxed sols.