Hydroxyapatite coating on Ti6Al4V alloy using a sol–gel derived precursor

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Abstract

A simple rapid-heating method was successfully developed for calcium phosphate coatings on Ti6Al4V substrates deposited by using a sol–gel derived precursor. After five repetitions of coating procedures and heat treatment at 600 °C, the formation of hydroxyapatite (HA) has been confirmed by X-ray diffractometry (XRD) analyses and the substrate material was found to be slightly oxidized. The residual organics, as revealed by X-ray photoelectron spectroscopy (XPS) spectra of a coating calcined at 400 °C, might retard the formation of calcium phosphate phase, thus only small amount of calcium phosphate phase is present. After calcining at 600 °C, calcium phosphate phase is the only one identifiable by XPS spectra. The adhesive strength of the five-coating layer on the substrate is around 60 MPa. The surface morphology of the thick HA film, calcined at 400 °C and then consolidated at 600 °C, displays porous structure arisen from rapid-heating of the bulk precursor. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydroxyapatite; Rapid-heating; Sol–gel coating; Porous structure; Ti6Al4V

1. Introduction

As the needs for fracture fixation and malfunction of hard tissues increases, there are large demands of metallic implants requiring suitable mechanical properties. For example, the Young’s modulus of such implants should be close to that of human bones so as to lessen the stress shielding effect [1] and to prolong the service life. The implants are made into various shapes including screws, plates, pins or others [2]. The most common material is the titanium-based alloy, which has been known as a tolerable metal in human body [3]. However, in order to enhance bone-inducing effect and to reduce healing time of the implanted hard tissues, the metallic implants are typically coated with biocompatible hydroxyapatite (HA, Ca10 (PO4)6 (OH)2) by means of a plasma spray technique [4], pulsed-laser deposition [5], electrodeposition [6], sol–gel processing [7–10] or others. Comparing to the required sophisticated vacuum systems and/or apparatus of the most methods, sol–gel processing is thought to be a relatively low-cost and easy method.

In the fabrication of HA-coated implants by the sol–gel method, processing parameters are extremely crucial especially the thermal processing parameters such as calcining temperature and duration, types of substrate, chemical compositions of the precursor, and number of HA coating layers. The adhesive strength, crystalline phases and biocompatibility of the resultant coatings are the most relevant issues in this kind of research. For the HA coatings on titanium-based substrates, the interaction between deposited film and substrate is always concerned so as to evaluate adhesive strength and phases formed. Generally, a rough surface [11] or a buffer layer of titanium oxide or CaTiO3 [12,13] is provided on the Ti-substrate surface in this regard. The thermal oxidation of metallic substrates is another factor to be considered and heating of titanium alloy at lower temperature has the advantage of low thermal stress. Therefore, researches are driven to the fabrication methods using low temperature processes such as sol–gel processing [9,10] or electrodeposition [6].

In the sol–gel processing, a low temperature calcining for HA coating on polished titanium alloy substrates has been preliminarily reported [9]. The precursor-coated titanium substrates are introduced into a 500 °C furnace for 15 min for calcination. It is known that oxidizing agent such as nitrate anions presented in the sol–gel precursor will help organics to be decomposed more easily using rapid-heating method, as also called combustion synthesis [14]. Therefore, processing temperature as well as residual organics in calcined coating will be lower. The present study deals with such an
In the present study, the HA coating was prepared from a precursor solution containing calcium nitrate tetrahydrate and triethyl phosphate (TEP). In order to reduce the possibility of substrate oxidation, rapid-heating was applied (at a ramp of 300 °C/min), to a temperature not higher than 600 °C on the precursor layer (pre-dried at 200 °C for 15 min) using an infrared furnace. The pull-out tests were then conducted for the adhesive strengths of the single-layer coatings. The X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were employed to analyze phases, surface chemical compositions, morphology and microstructure of the cross-section.

2. Experimental

2.1. Deposition of coating

The preparation of the precursor was done by mixing Ca(NO₃)₂·4H₂O (98%, Ferak Laborate, Germany) and (C₂H₅O)₃PO (99%, Janssen Chemicals, Belgium) in 2-methoxy ethanol (ACS grade, TEDIA Chemicals, USA). Upon aging, the as-prepared solution was closely capped, and was placed in an oil bath set at 80–90 °C. Upon gelation (drying), the solvent was evaporated in the same oil bath for 4 h so that a viscous precursor was obtained. The viscosity of the precursor at 25 °C was measured by a cone-and-plate viscometer (Brookfield DVIII+, USA) with a measurement range from a few cP to 10⁵ cP. The precursor was a Newtonian fluid and during gelation from 1 to 6 h, the viscosity was increased from 7 cP to more than 10⁵ cP. For the precursor dried for 3–4 h, the viscosity falls in 14–23 cP, depending on the exact room temperature during the gelation.

The calcium phosphate coating was deposited by layer by layer as follows. Firstly, Ti6Al4V alloy substrates (around 10 mm × 10 mm), being blasted with alumina beads of 500–850 μm particle size, and washed twice in acetone and isopropanol, were dip-coated with a viscous precursor (viscosity 15 cP at 25 °C) at a withdrawal rate of 2.3 mm/s. Spin coating (1500 rpm) was also done on the substrates for the first-layer coating using the same precursor. Secondly, the precursor/substrate was pre-dried at 200 °C for 15 min. Finally, dried samples were rapid-heated in an infrared furnace to 400 °C, using a ramp 300 °C/min and holding for 1 min at 400 °C. The coating was repeatedly deposited for another four times. To consolidate the above thick film, the total coating was subjected to a rapid-heating (300 °C/min) to 600 °C and holding for 1 min. In order to observe oxidative reaction of the substrate, a blank substrate (without precursor) was also rapid-heated at 400 and 600 °C, respectively.

2.2. Pull-out tests

The adhesive strengths of the first-layer coating, fabricated by either dip coating or spin coating were measured by a pull-out test method [11]. An epoxy glue applied on the surface of the coating connects it and a stud bar (2.69 mm in diameter). The epoxy glue was then cured at 180 °C for 2 h. A tensile test was then run. A computer records the breaking forces of the specimens and calculates the adhesive strength of the coatings.

2.3. XRD, SEM and XPS analyses

XRD patterns were taken from samples using a wide-angle X-ray powder diffractometer (model D/max-III, Rigaku Co., Japan). X-ray radiation Cu Kα1 (1.5405 Å) is set at 30 kV and 20 mA. The crystalline phases were identified using the JCPDS files (HA: 09-0432; CaCO3: 47-1743; TiO2: 21-1276; α-Al2O3: 05-0712). Film morphology and cross-sections were observed using a scanning electron microscope (model JSM-5410, Japan Electron Optics Laboratory, Japan). The XPS measurements were carried out using a PHI 1600 instrument (Perkin-Elmer Corporation). The spectrophotometer employed monochromatic Mg Kα X-ray source (hν = 1253.6 eV) operated at 15 kV and an ambient pressure 10⁻⁶ Torr. The instrumental resolution was estimated to be 0.1–0.8 eV. The binding energy (BE) scale of all XPS spectra was corrected by using sputter-cleaved Cu 2p/3 (BE = 932.7 eV) and a value of 3.0 eV was subtracted from the observed BE values for Ca, P and O.

3. Results and discussion

3.1. The crystalline structure and the layer structure

An XRD pattern of a blasted substrate is shown in Fig. 1(a). The major phases are titanium and α-Al2O3; that is due to the entrapment of alumina debris on the substrate during bead blasting. Fig. 1(b) shows an XRD pattern of an HA coating with five coated layers, consolidated at 600 °C. Characteristic HA peaks can be found from diffraction peaks at angles (2θ) in the range 25–35°. Besides HA peaks, minor surface oxidation of titanium can also be observed. The CaCO3 phase in the coating might be due to the combination of calcium in the precursor with evolved CO2 arising from pyrolysis of organics in precursor during heating [15]. The blank substrates subjected to rapid-heating at 400 or 600 °C show no apparent oxides of Ti, as in Fig. 1(c) or (d). Additionally, one can see in XRD patterns that the line widths of the substrate phases are slowly decreasing, meaning thermal energy leads to grain growth in the substrate.

In sol–gel coating of HA onto titanium substrate, the adhesion to substrates is closely related to substrate surface compositions and surface roughness. TiO2 (either rutile or anatase) and CaTiO3 (perovskite) [12,13] have been...
Fig. 1. XRD patterns of (a) a blasted substrate surface; (b) a five-layer coating, calcined at 400°C after each coating and consolidated at 600°C as a whole; (c) a blank substrate subjected to rapid-heating at 400°C and (d) heated at 600°C (H: HA; C: CaCO₃; S: substrate; T: TiO₂; A: α-Al₂O₃).

Fig. 2. SEM micrographs of (a) a cross-sectional view of the first coating layer, calcined at 400°C; (b) Ti6Al4V substrate surface blasted with α-Al₂O₃ beads; (c) the outermost surface of the five-layer coating, calcined at 400°C after each coating and (d) the five-layer coating consolidated at 600°C.
weaken this effect so that a lower adhesive strength is obtained.

Due to the strong adhesive strength of the resultant first-layer coating, chemical reactions are believed to occur at the interface when a single layer precursor was coated on titanium alloy and heat treated. This retards HA phase formation on the one hand and enhances the adhesive strength on the other. HA phase is manifest only in thick coating layers as shown in XRD pattern for layers with five coatings (Fig. 1(b)).

The reported reactions between titanium and phosphates (forming Ti₄P₃ [16,17]) and calcium (forming CaTiO₃) at the coating/substrate interface can be found in literature. The former case results in coatings with a higher Ca/P ratio, and vice versa in the latter case. In our study, it is speculated that certain amorphous Ti–Ca–P–O compounds have formed at the low heat treatment temperature (400 °C) adopted leading to the observed much enhanced adhesive strength.

3.2 XPS characterization of coatings

A surface sensitive XPS technique was applied to study the surface properties of the as-calcined coatings heated by the rapid-heating method. Figs. 3 and 4 display the Ca 2p and P 2p XPS spectra of the first-layer coating, calcined at 400 and 600 °C, respectively. The identified peaks and their associated reference values are summarized in Table 1. The O 1s spectra for the two coatings are not shown in the figures but corresponding peak values are listed in Table 1. For the 400 °C-calcined coating, the O 1s signal, peaking at
529.8 eV is a typical value for that of calcium phosphate materials (CPM) [18,19]. The Ca signals (Fig. 3(a)) correspond to 2p_{1/2} and 2p_{3/2}, and can be attributed to CPM. There is a P O 4 2p peak signal at 133 eV, shown in Fig. 3(b). This could also be identified as the signal from CPM. Another peak at 130.4 eV is a lower value as compared with BE values of CPM in literatures. This could be attributed to phosphorus–Ti (the substrate) reaction. Fig. 4 displays the XPS spectra Ca 2p, P 2p and O 1s explicitly show the characteristics of CPM. Here CPM is assigned, rather than HA, because typical XRD pattern of HA is still not shown. It is speculated that the CPM is amorphous. Additionally, the wide scan spectra (BE = 0–1000 eV, not shown here) indicate that intensity of C 1s peak for the 600 °C-calcined coating is lower than that of C 1s peak for the 400 °C-calcined one. This means that more residual organics are still present in the 400 °C-calcined coating and the formation of CPM phase is retarded by these organics. The phosphorus atoms might be incorporated in the organic network so that XPS measures two environments, which are CPM environments and the organo-phosphorus one. A comparison of the XPS results for these two calcining temperatures suggests that rapid-heating and soaking at 400 °C might not be able to convert the coating to high-quality HA layer but could be so at 600 °C, in case, enough thickness of the coating is provided.

3.3. Morphology of coatings observed by SEM

Fig. 2 shows SEM micrographs of coatings fabricated by dip coating method. Fig. 2(b) is an SEM micrograph of Ti6Al4V substrate blasted with Al2O3 beads. Comparing with the rough surface of the substrate, the outermost surface of the coating (Fig. 2(c)) has been covered with a smoother coating. After initial calcining at 400 °C, the coating was further consolidated at 600 °C in order to reduce residual carbon at the one hand and to densify the whole coating on the other. The morphology, shown in Fig. 2(d), looks like spherical particulars glued on dense CPM coating resulting in a porous surface. Because of the rough substrate surface, there exists some crater areas that fill with more precursors and the morphology of calcined deposits in these areas is porous. The formation of this porous structure might be similar to that of rapid-heating bulk precursor [14]. When large amount of precursor is heated and interface reaction does not take place, the uppermost surface behaves like the bulk precursor. Therefore, one can expect that regular craters distributed on uppermost surface might be useful to tailor porous structure of the coatings, as long as rapid-heating processing can be tuned to minimize residual carbon. But it should be noted that in some surface regions, the blasted substrate has low-lying grounds with 15 μm in depth. Thickness less than 3 μm is found in these regions. However, the resultant film is much stronger than the cracked films deposited on surface-polished Ti substrates, even at a low calcining temperature (500 °C), adopted in literature [19].

For biocompatible implants, the existence of HA is the major concern. Furthermore, controlled porosity is always required because living cells need a proper scaffold to proliferate and nutrition can be supplied as cells migrate into the porous space [20]. Osteoblasts, the bone forming cells, mature at a diameter size of 10 μm whereas the inter-particulate space shown in Fig. 2(d) is around 10–20 μm. Owing to this size relationship, the biocompatible coating developed in this study will be suitable for cell proliferation and might be helpful for the in-growth of tissue, such as blood vessels.

4. Conclusions

A simple rapid-heating method has been successfully developed to fabricate HA coatings on Ti6Al4V substrates using a sol–gel precursor. XPS P 2p spectrum of the first HA coating layer calcined at 400 °C indicates that there exists a product of interfacial reaction, peaking at 130.4 eV, as well as a minor CPM. As calcining is performed at 600 °C, the same first-layer coating exhibits CPM only. Thus, interfacial reactions between the precursor and the substrate leads to possible amorphous Ti–Ca–P–O phases during the heating at 400 °C to account for the observed high adhesive strength (90 MPa). However, the five-coating layer is relatively thick. As a result, the strength decreases (60 MPa). XPS analyses show manifest amount of residual organics leading to the retarded formation of CPM in the coating calcined at 400 °C.

For apparent HA phase to be observable in the XRD pattern, five-coating layers calcining at 400 °C then subsequently consolidated at 600 °C are required. In the adhesive strength tests of the first coating layer, either spin coating or dip coating, the breakages occur at glue-coating interface representing an adhesive strength higher than 90 MPa. Thus, the first-layer is firmly adhered to the substrate. A porous structure is formed on the outermost coating surface with a pore size 10–20 μm by the current method. This structure is due to the fast decomposition during rapid-heating the precursor deposited on the substrate, and is very suitable for in-growth of living cells.

Table 1

<table>
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<tr>
<th>Cont level</th>
<th>Measured BE value</th>
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<tr>
<td></td>
<td>Calculated at 400 °C</td>
<td>Calculated at 600 °C</td>
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<tr>
<td>Ca 2p_{3/2}</td>
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<td>350.8</td>
</tr>
<tr>
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<tr>
<td></td>
<td>0.4</td>
<td>–</td>
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<tr>
<td>O 1s</td>
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<td>531.4</td>
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Acknowledgements

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References